Generalized spin precession equations

Hans-Jürgen Stöckmann¹ and Dirk Dubbers²

¹ Fachbereich Physik der Philipps-Universität Marburg, Renthof 5, D-35032 Marburg, Germany
² Physikalisches Institut der Universität Heidelberg, Im Neuenheimer Feld 226, D-69120 Heidelberg, Germany
E-mail: stoeckmann@physik.uni-marburg.de and dubbers@physi.uni-heidelberg.de

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Abstract
The Bloch equations, which describe spin precession and relaxation in external magnetic fields, can be generalized to include the evolution of polarization tensors of various ranks in arbitrary multipole fields. We show applications of the generalized spin precession equations using simple examples from atomic, nuclear and condensed matter physics, and compare the various approaches found in the literature. The derivation of the generalized Bloch equations can be considerably simplified using a particular bra–ket notation for irreducible tensors.

Keywords: Bloch equations, Liouville master equation, nuclear magnetic resonance, relaxation, spin precession

1. Introduction

The Bloch equations [1] describe the response of the magnetization \( M \) of an ensemble of particles to a classical magnetic field \( B \), for the case where the magnetization returns exponentially toward its equilibrium value \( M_0 \),

\[
\begin{align*}
\dot{M}_x &= \gamma (M \times B)_x - M_x / T_1, \\
\dot{M}_y &= \gamma (M \times B)_y - M_y / T_1, \\
\dot{M}_z &= \gamma (M \times B)_z - (M_z - M_0) / T_1,
\end{align*}
\]

with gyromagnetic ratio \( \gamma \) and longitudinal and transverse relaxation times \( T_1 \) and \( T_2 \).
We can also write the Bloch equations in terms of the vector polarization
\[ P = \langle J \rangle / j, \]  
with angular momentum expectation value \( \langle J \rangle \) and quantum number \( j \), and with \( M = n\mu P \) for particles of number density \( n \) and magnetic moment \( \mu = -\hbar \gamma j \). For negligible relaxation \( T_1, T_2 \to \infty \), the Bloch equations then reduce to the simple \textit{spin precession equation}
\[ \dot{P} = P \times \omega_p, \]  
with the Larmor angular frequency vector \( \omega_p = \gamma B \). This equation holds for arbitrary \( j > \frac{1}{2} \), and is all one needs for a complete quantum description of this simple system. Equation (3) is called semiclassical only because the external field \( B \) is not quantized.

While equations (1) and (3) were originally derived in the context of magnetic resonance, it was soon recognized that they describe the evolution of any system with ‘effective’ or ‘pseudospin’ \( J \). The best known examples are the maser [2], and the two atomic states involved in an optical transition [3, 4], in which the latter obey the ‘optical Bloch equations’, both systems having effective spin-½. Even multiple-quantum transitions are covered by these equations.

It is well known that for (pseudo-)spin \( j > \frac{1}{2} \), the polarization vector \( P \) is not sufficient to describe the state of the system, and higher ranks \( \rho_L \) of spin polarization must be included [5, 6]. The \( \rho_L \) are called statistical or polarization tensors, or state multipoles, with components \( \rho_{LM} \), \( M = -L, \ldots, L \). The rank-1 polarization \( \rho_1 \) is called a \textit{vector polarization} or \textit{orientation}, and the rank-2 tensor \( \rho_2 \) an \textit{alignment}, with components as listed in equations (A.1) and (A.3) of the appendix.

The Bloch equations (1) can be generalized to include the evolution of the polarization tensors \( \rho_L \) in the presence of arbitrary multipole fields. The interactions of these fields with the corresponding multipole moments of the particles are described by some tensorial sets of interaction frequencies \( \Omega_L \). The magnetic dipole interaction is given by a vector \( \Omega_1 \), the electric quadrupole interactions by a tensor \( \Omega_2 \), with frequency components \( \Omega_{LM} \) as listed in equations (A.5). The general definitions of the tensors \( \rho_L \) and \( \Omega_L \) will be postponed to section 4.

Using these quantities we can replace equation (3) by the \textit{generalized spin precession equation}
\[ \dot{P} = \sum_{L_1, L_2} C_{L_1, L_2} \left[ \Omega_{L_1} \times \rho_{L_2} \right], \]  
which holds in the limit of negligible relaxation. These equations had been derived by Fano in an important paper [7], which regrettably never found the recognition it deserves. A possible explanation for this may be that [7] uses an unfamiliar notation, and that the derivation therein is technical and tends to obscure the essential underlying ideas.

The tensor products in equation (4) are the generalization of the vector product \( P \times \omega_p \) in equation (3), and are defined by the bilinear forms [8, 9]
\[ \left[ \Omega_{L_1} \times \rho_{L_2} \right]_{LM} = \sum_{M_1 M_2} \langle L_1 M_1 | L_2 M_2 \rangle \langle LM \rangle \Omega_{LM_1} \rho_{L_2 M_2}. \]  
The \( \langle L_1 M_1 | L_2 M_2 \rangle \) therein are Clebsch–Gordan coefficients for the ranks of the tensors involved. Hence, the tensors \( \Omega_{L_1} \) and \( \rho_{L_2} \) couple to each other in the same way as ordinary orbital angular momentum operators \( L_1 \) and \( L_2 \). In particular, they obey the triangular relations.
\[ |L_1 - L_2| \leq L \leq L_1 + L_2 \text{ and } M = M_1 + M_2. \] The coefficients \( c_j \), to be derived in section 4, limit these ranks to \( L_1, L_2, L \leq 2j \). Hence spin \( j = \frac{1}{2} \) particles can only have a vector polarization \( \rho_1 \) and magnetic dipole interactions \( \Omega_1 \), while spin \( j = 1 \) particles can also have an alignment \( \rho_2 \) and electric quadrupole interactions \( \Omega_2 \). The coefficients \( c_{j}(L_1 L_2 L) \) for magnetic and quadrupole interactions \( L_1 = 1, 2 \) are given by equations (A.8) and (A.9) for arbitrary values of \( j, L_2, \) and \( L \).

To include relaxation, we extend Fano’s equation to obtain the generalized Bloch equation

\[
\dot{\rho}_{LM} = \frac{i}{\tau_{LM}} \sum_{L_1, L_2} c_j (L_1, L_2, L) \left[ \Omega_{L_1} \times \rho_{L_2} \right]_{LM} - \frac{\rho_{LM} - \rho_{LM0}}{\tau_{LM}} , \tag{6}
\]

which holds under conditions that will be discussed in section 5. In thermal equilibrium there may be nonzero polarization components \( \rho_{LM0} \) (usually limited to the \( M = 0 \) components), analogous to \( M_{z0} \) in equation (1). For the special case that particles with spin \( j \geq \frac{1}{2} \) carry a pure vector polarization \( \rho_1 \) and interact solely with a uniform magnetic field, equation (6) reduces to the Bloch equations (1), where we identify \( \tau_{10} \) and \( \tau_{1 \pm 1} \) with \( T_1 \) and \( T_2 \), respectively.

The purpose of the present paper is twofold. First we want to popularize this pictorial and most natural generalization of the spin precession equations. Indeed, while the Bloch equations are among the most frequently cited equations in physics (more often than the Einstein 1905 or the Heisenberg or Schrödinger 1925 papers), we have not found equations (4) or (6) reproduced anywhere, either in recent textbooks on tensors and density matrices, see for instance \([6, 9, 10]\), or in scientific journals, see the citations in section 3, and references therein.

Certainly, the generalized precession equations are implicitly contained in more complicated theoretical expressions found in the specialized literature, and we do not propose to have equation (6) replace the highly developed codes used to calculate more complicated signal shapes in atomic spectroscopy or in nuclear magnetic resonance (NMR). However, the specialized papers in these fields require a high entrance fee that we intend to lower considerably by using a physically more palpable approach, based on the analogy with the well known Bloch equations. For easy access, in section 2 we start with a number of examples of applications from diverse fields of spectroscopy on polarized spin ensembles. In section 3 we shall compare the various possible approaches to spin precession, and we postpone our survey of the literature to this section.

The second purpose of the present paper is to show that the derivation of these generalized equations can be considerably simplified by using a special bra–ket notation for the tensors. In section 4 we show that the derivation of Fano’s equation (4) from Liouville’s equation can be reduced to a small number of simple steps. In section 5 we apply the same technique to derive the relaxation term in equation (6), which again only needs a few steps, whereas the same treatment in standard textbooks \([11–13]\) usually requires many pages of technically challenging text.

## 2. Applications

Before we go into further details, let us list some of the applications of the generalized spin precession equations. Some of the examples given in the following are discussed in more detail in a recent book by the present authors \([14]\). In principle, the statistical tensors \( \rho_L \) are needed in all quantum calculations of spin-dependent interactions of particles, in particular in studies of the angular distributions or correlations of particles emitted in nuclear, atomic, or molecular
reactions, see for instance chapter 19 of [15] or section 20.5 of [14]; for earlier work see also [16]. These distributions can be written in terms of the elements of the rotation matrices $D_{MM'}^L$, for the case of a rotationally symmetric configuration for instance as

$$ W(\theta) = \sum_L r_L \rho_{L,0} P_L(\cos \theta) \tag{7} $$

with Legendre polynomials $P_L = D_{00}^L$, the angle $\theta$ towards the symmetry axis, and some coefficients $r_L$.

Under the action of external electromagnetic fields, the polarization components evolve as given by equation (6), and with $\rho_{LM}(t)$ the corresponding angular distribution of type (7) also becomes time dependent. This is a standard situation met in atomic spectroscopy, in nuclear and atomic magnetic resonance, and in the field of nuclear-radiation-detected perturbed angular correlations (PAC) or distributions (PAD), traded under the names $\gamma$-PAD, $\gamma\gamma$-PAC, $\beta$-NMR, $\mu$-SR (for muon spin rotation), etc, which are useful tools for measuring the internal fields in condensed matter; see [17] for a survey and for further references.

For the sake of simplicity, we regard a spin-1 system, where the tensor ranks are limited to $2j=2$. Equation (4) then reduces to

$$ \dot{\rho}_1 = -i \left[ \Omega_1 \times \rho_1 \right]_1 + i \sqrt{3} \left[ \Omega_2 \times \rho_2 \right]_1, \tag{8} $$
$$ \dot{\rho}_2 = -i \sqrt{3} \left[ \Omega_2 \times \rho_1 \right]_2 - i \sqrt{3} \left[ \Omega_1 \times \rho_2 \right]_2. $$

We write the precession equation (4) in short form as

$$ \dot{\rho} = i \hat{L} \rho. \tag{9} $$

In the case $j=1$, equation (8), we have the row vector $\rho = (\rho_1, \rho_2)^T$, while the 8 × 8 so-called Liouville matrix $\hat{L}$ is given by equations (A.10) to (A.12).

Often only the time average solution

$$ \bar{\rho} = \frac{1}{\tau} \int_0^\infty \rho(t) e^{-i \tau t} dt \tag{10} $$

over the lifetime $\tau$ (or over a single relaxation time) of the system is of interest. From this, for time-independent $\hat{L}$, the time average of $\dot{\rho}$ is obtained from equations (10) and (9) through integration by parts as $\bar{\rho} = i \hat{L} \bar{\rho} = [\dot{\rho} - \rho(0)]/\tau$, which leads to the solution

$$ \bar{\rho} = \left( I - i \tau \hat{L} \right)^{-1} \rho(0), \tag{11} $$

with unit matrix $I$.

First we study the purely magnetic dipole case, with only $\Omega_1 \neq 0$. In this case the $\rho_L$ are decoupled from each other, i.e. the Liouville matrix $\hat{L}$ is block diagonal with respect to rank $L$, and we have $\dot{\rho}_L = i \hat{L}_{LL} \rho_L$, with $L=1,\ldots,2j$. The elements of the diagonal submatrices $\hat{L}_{LL}$ turn out to be independent of $j$. With this, the following examples from atomic and nuclear physics can be treated.
2.1. Atomic double resonance \[18\]

Unpolarized spin-1 photons have substate \(m\) populations \(p_{+1} = p_{-1} = \frac{1}{2}\) and \(p_0 = 0\). They hence carry a natural alignment \(\rho_{20} = \sqrt{1/6} (1 - 3p_0) = \sqrt{1/6}\) with respect to their line of flight along axis \(z\), see equation (A.3). Upon resonant photon absorption by unpolarized atoms, due to angular momentum conservation, this alignment is carried over as \(\rho_{20}(0)\) to the excited atom of lifetime \(\tau\). When the atoms are exposed to a uniform external field \(B_z\), a radiofrequency (rf) field of amplitude \(B_x \cos \omega t\) can induce resonance transitions between the excited atoms’ Zeeman levels. We use the rotating frame approximation and replace \(B_z\) in \(\hat{L}_{22}\) by the effective field component \(B_{\text{eff}} = (\omega - \omega_0)/\gamma\), with \(\omega_0 = \gamma B_z\). Using equation (11), the inversion of \(\hat{I} - i\gamma \hat{L}_{22}\) by means of computer algebra then gives the typically double-humped double resonance formula

\[
\tilde{\rho}_{20} = \left[ 1 - \frac{3\beta^2}{\zeta^2} \left( \frac{\delta^2}{1 + \delta^2} + \frac{\beta^2}{1 + 4\delta^2} \right) \right] \rho_{20}(0),
\]

valid for any (effective) spin \(j\), with the following parameters: \(\delta = (\omega - \omega_0)\tau\) for the detuning; \(\beta = \omega_1 \tau = \gamma B_x \tau\) for the rf-amplitude; and \(\zeta = (\delta^2 + \beta^2)^{1/2}\) for the effective field amplitude. The double resonance signal, shown in figure 1 for \(\omega_1 \tau = 2\), can be detected via the reemitted light. At resonance, light intensity emitted in a certain direction, as given in equation (7), follows the shape of \(\tilde{\rho}_{20}(\omega - \omega_0)\) shown in figure 1.

2.2. Hanle effect \[19\]

If the atomic alignment is produced in the presence of a transverse static field \(B_x\), the initial alignment \(\rho_{20}(0)\) will start precessing about this field up to the time of decay. In a weak magnetic field, the alignment has no time to precess before the atom decays, while in high field, after many precessions, its time average decreases considerably. The Hanle signal, centered at zero field, is obtained for arbitrary \(j\) in the same manner as above to

\[
\tilde{\rho}_{20} = \frac{1 + \gamma^2 B_x^2 \tau^2}{1 + 4\gamma^2 B_x^2 \tau^2} \rho_{20}(0).
\]
Next we study an electric quadrupole interaction $\Omega_2 \neq 0$, which, in contrast, couples a polarization tensor $\rho$ to the tensors $\rho_{L \pm 1}$ of neighboring ranks. For $j = 1$, for example, the vector polarization $\rho_1$ couples to the alignment $\rho_2$, see equation (8). Therefore the submatrices $\hat{L}_{12}$ and $\hat{L}_{21}$, equations (A.12) come into play, and with it the following experiments become accessible.

### 2.3. Nuclear reorientation and decoupling

For $j = 1$, a quadrupole interaction along principal axes in constant field $B_z$ couples an initial pure longitudinal polarization $\rho_{10}(0)$ solely to the transverse alignment components $\rho_{2 \pm 2}$,

$$
\dot{\rho}_{10} = i q (\rho_{22} - \rho_{2-2}),
$$

$$
\dot{\rho}_{2 \pm 2} = \mp i \left( b \rho_{2 \pm 2} + q \rho_{10} \right),
$$

with $b = \gamma B_z \tau$ and $q = \eta \omega_Q \tau$, and with quadrupole frequency $\omega_Q$ and asymmetry parameter $\eta$ as defined in (A.6) and (A.7), while an initial longitudinal alignment $\rho_{20}$ remains unaffected. Inversion of a $3 \times 3$ matrix then gives the time average solutions

$$
\bar{\rho}_{10}(B_z) = \frac{1 + 4b^2}{1 + 4q^2 + 4b^2} \rho_{10}(0),
$$

$$
\bar{\rho}_{2 \pm 2}(B_z) = \frac{\sqrt{2} (2b \pm i) q}{1 + 4q^2 + 4b^2} \rho_{10}(0).
$$

At intermediate field strengths, part of the initial polarization is converted into an alignment, a process that we call reorientation. At high field $\gamma B_z \gg \omega_Q$, the quadrupole interaction is decoupled and the original polarization is restored, as shown in figure 2.

### 2.4. Steady-state NMR

NMR in the presence of electric quadrupole interactions is widely used, for instance in deuteron NMR. Figure 3 shows the nuclear polarization for NMR in the presence of a rotationally
symmetric electric field gradient ($\eta = 0$) for the case of a $j = 1$ nucleus in a single crystal. Again we used equation (11) with the appropriate matrix $\hat{L}$ in the rotating frame. We inserted the parameters used in the $\beta$-NMR experiment on oriented nuclei as described in [21], and added their data to figure 3. One finds two quadrupole-split one-quantum transitions ($|\Delta m| = 1$) at $\omega = \omega_0 \pm 3\omega_Q$, and one two-quantum transition ($|\Delta m| = 2$) at $\omega = \omega_0$. Due to its low transition probability, the two-quantum signal is very narrow.

2.5. Free induction decay

Another NMR application is free induction decay (FID) after pulsed resonant magnetic excitation. A π/2-radiofrequency pulse turns an equilibrium polarization $P_z(0)$ into a transverse polarization $P_y(0) = i[\rho_{11}(0) + \rho_{1-1}(0)]$, for $j = 1$, whose spin precession is then observed (this is called quantum beats in other contexts). This FID signal is easily derived from equation (8) because the transverse polarization component $\rho_{11}$ only couples to the alignment component $\rho_{21}$, and $\rho_{1-1}$ only to $\rho_{2-1}$. One finds a superposition of two oscillations of frequencies $\Omega_\pm$ and amplitudes $A_\pm$,

$$\Omega_\pm = \omega_\pm \pm \left(\omega_\pm^2 + 9\omega_Q^2\right)^{1/2}, \quad A_\pm = 1 \pm \omega_\pm/\sqrt{\omega_\pm^2 + 9\omega_Q^2},$$

with $\omega_\pm = (\sqrt{2} \pm 1) \omega_Q/2$.

2.6. Angular dependences

Polarization signals as a function of the direction of the applied fields are accessible as well, in general using computer algebra, though we do not go into these details here.

All the above results, linking rather different fields, are obtained with a single standard math program with matrix $\hat{L}$ as the input and a few lines of code.
3. The various approaches to spin precession

The starting point of all calculations on spin precession is the Liouville equation [9, 22]
\[
\dot{\rho} = i\left[\rho, H\right]
\]  
(17)
for the density operator \(\rho\) of rank \(2j+1\), with matrix elements \(\langle jm|\rho|jm'\rangle\). The irreducible elements \(\rho_{LM}\) of the density operator are obtained from its Cartesian components by
\[
\rho_{LM} = \frac{2L + 1}{2j + 1} \sum_{mm'} \langle jm|\rho|jm'\rangle \langle jm'LM|jm\rangle.
\]  
(18)

Equations (17) and (4) are mathematically equivalent, but, as the examples in section 2 show, the irreducible spin precession approach via the \(\rho_{LM}\) has a number of obvious advantages that we summarize as follows.

(i) Irreducible tensors permit the most compact coordinate-free and therefore most pictorial presentation of physics results.

(ii) The statistical tensors \(\rho_L\) allow a direct interpretation in terms of polarization, alignment, etc. Very often just one tensor component is prepared in the production of the ensemble, all other initial components being zero. The spin precession equation is ideally suited to cope with this situation.

(iii) The tensor products allow an easy visualization of what is going on. From the selection rules of the Clebsch–Gordan coefficients and the prefactors \(c_j\) (for the latter, see equations (38), (39) and (A.8) (A.9) below), it is obvious that a magnetic interaction can only change the \(M\) state of a tensor component, but never its rank \(L\), whereas a quadrupole interaction always changes the rank by \(\pm 1\), as exemplified in equation (8).

(iv) If there are symmetries, for instance rotation symmetry about the axis of an external magnetic field, the system of generalized spin precession equations with \((2j+1)^2-1\) variables will decompose into a smaller set of uncoupled differential equations.

(v) Another decisive advantage of the spin precession picture is that the problem is separated into three independent steps. 1. The preparation of the initial state \(\rho(0)\), for instance via particle absorption or emission, or via steady-state Boltzmann polarization. 2. The response \(\rho(t)\) of the system to external perturbations. 3. The detection of this response, for instance via the angular distributions of reaction products, as in equation (7). The response \(\rho(t)\) or \(\bar{\rho}\) can therefore be calculated once and for all, independent of the particular processes chosen for the initial spin polarization or for the final spin analysis.

Although the generalized Bloch equation (6) is not explicitly used in the literature, many calculations arrive at results identical to ours. In the following we describe some of the alternative routes used in the literature.

3.1. Atomic and nuclear physics

We begin with the steady-state polarization effects in atomic physics. Hanle [19] explained the effect that carries his name via the movement of an elastically bound classical electron in a magnetic field, although he was aware that the effect required some quantum treatment. Today, standard atomic physics textbooks [23, 24] describe such spin precession effects as an
interference phenomenon between different amplitudes of the emitted light, which are then coherently summed over the unobserved atomic $m$-substates involved.

This description in terms of interference is perfectly correct, though the advantages of the irreducible representation listed above are lost. The two seemingly unrelated pictures, the spin rotation picture mainly used in nuclear physics, and the interference picture mainly used in atomic physics, have peacefully coexisted over many years, without taking much notice of each other, although there was an early discussion on the relations between the two approaches [25, 26].

The atomic double resonance formula (12), on the other hand, had first been derived by Brossel and Bitter [18], again after lengthy summations over unobserved atomic substates using Majorana’s formula for the individual rf-transition probabilities [27, 28]. The method is rather uneconomical because the resonance signal must be derived separately for every value of angular momentum number $j$, despite the rule that magnetic spin precession is independent of $j$.

In more recent times, the spin precession picture has entered atomic physics too [6], though again without explicit recourse to equation (4). The ground-state Hanle effect in the alkaline hyperfine structure was recently treated thoroughly in terms of the $\rho_{LM}$ [29]. The general result for the Hanle signal, equation (8) of [29] obtained using computer algebraic methods, reduces to our equation (13) for $\tau_{10} = \tau_{20} \equiv \tau$ and $B = B_c$. The same method was applied to derive the line shapes of the atomic double-resonance signals [30].

Atomic reorientation under the combined action of magnetic and electric fields was investigated in [20]. An initial transversal rank-2 alignment of alkaline atoms created by photon absorption in a spin-0 to spin-1 transition was converted via an induced atomic quadrupole moment into a rank-1 polarization. The magnetic-field dependence of this ‘alignment-to-orientation conversion’, or AOC, was calculated in [20] using a Hamiltonian approach. Our Liouville approach, equation (14), gives the same result, namely equation (15) and figure 2 (derived for the inverse ‘OAC’ process), but with the alignment and polarization exchanged. Such AOC effects can also be induced by strong laser fields [31]. Similar atomic polarization effects, induced by atomic collisions, are reviewed in [32]. For a nuclear OAC experiment, see [33].

The relation between the above mentioned magnetic-field-induced polarization effects and the classical magneto-optical Faraday effect, dichroism, or birefringence, are elucidated in [34]. Furthermore, a new method for visualizing atomic polarization tensors is presented by drawing a surface in three dimensions representing angular momentum density; see also [35].

Nuclear-radiation-detected NMR, based on oriented nuclei, is identical to atomic double resonance: after all, it makes no difference whether light rays emitted by atoms or $\gamma$-rays (or other particles) emitted by nuclei are used for signal detection. In a rather lengthy procedure, Matthias et al [36] derived the equations of motion of the irreducible components $\rho_{LM}$ for these cases. These authors first expressed general results, via equation (18), as sums over $m$, $m'$ and $j$-dependent coefficients, and then contracted these for the special case of purely magnetic interactions, using well-known sum rules.

The same procedure of $m$-dependent perturbation coefficients is often used in more general PAC studies involving additional electric quadrupole interactions [17]. Indeed, for systems of both high values of $j$ and low or no symmetry, the computation of a vast number of $m$, $m'$-dependent coefficients (namely, the wavefunctions), obtained by diagonalizing a Hamiltonian of rank $2j+1$, may frequently require less computing power than the handling of a Liouvillian of rank $(2j+1)^2 - 1$. However, even in these cases it is advisable to first turn to the irreducible
representation and inspect Fano’s spin precession equation in order to find out which polarization elements, $\rho_{LM}$, are coupled to each other before reverting to the less conspicuous angular momentum representation. In any case, with steadily growing computing power, and with equally increasing use of time-resolved instead of frequency-resolved experimental techniques, the balance seems to shift more and more from the Hamilton-based to the Liouville-based approach.

Different approaches also exist for the time-dependent solutions. In atomic physics, the so-called quantum beats are usually described as an interference phenomenon [23, 24]. Let an excited atomic state display a small energy splitting $\delta E$, and let this state be excited with a short pulse of light of duration $\Delta t$. Let the splitting $\delta E$ of the two levels be so small that it is blurred by the energy uncertainty $\Delta E$ of the incoming laser pulse, that is, $\delta E \ll \Delta E = \hbar/\Delta t$. (19)

In this case it is uncertain which of the two upper states was excited, and hence the amplitudes of the emitted light must be added coherently, leading to a beating of the light intensity at frequency $\omega_0 = \delta E/\hbar$. [23, 24]

In nuclear physics, these quantum beats are usually described as a spin (or pseudo-spin) precession of the excited state [17]. The state is prepared by some nuclear reaction, taking place within a time interval $\Delta t$ short enough that the state’s initial transverse polarization does not dephase during the preparation process. This leads to the phase requirement $\delta \varphi = \omega_0 \Delta t \ll 1$. (20)

With $\Delta t = \hbar/\Delta E$, that is, $\delta \varphi = \delta E/\Delta E \ll 1$, this requirement is identical to (19).

3.2. Nuclear magnetic resonance

A vast body of literature also exists on NMR and spin relaxation in condensed matter. Such conventional NMR is usually limited to polarization rank $L = 1$, both for the initial Boltzmann polarization $\rho_{10}(0) \sim 10^{-5}$ and for the final detection of magnetization, $M \propto \rho_1$, although the latter signal also depends on intermediate reorientations involving higher ranks, $\rho_{L>1}$. The occurrences of off-diagonal elements, i.e. $\rho_{LM}$ with $M \neq 0$, are often called coherences of the system. Magnetic resonance imaging (MRI) with optically pumped nuclei that carry a sizeable polarization $\rho_{10}(0) \sim 1$ [37], on the other hand, mainly involves the $j = \frac{1}{2}$ isotopes $^3$He, $^{13}$C, and $^{129}$Xe that can only possess a vector polarization $\rho_1$ anyway.

Let us now retrace the history of irreducible tensors in NMR. The majority of standard textbooks on NMR [38–40] do not make use of irreducible tensors, or only mention them briefly [41]. The Wigner–Eckart theorem, for instance, is quoted only in the classical NMR monographs by Abragam [12] and Slichter [11], and in Mehring’s book [42]. The classical 1948 ‘BPP’ paper on relaxation in NMR [43] still worked with transition probabilities $W_{m \rightarrow m'}$ between neighboring magnetic substates. In 1965, Redfield [44] based relaxation theory on density matrices and correlation functions, and derived the relaxation matrix for fluids in the extreme motional narrowing approximation, i.e. for very short correlation times of the magnetic fluctuations of the system under study.

Next, in 1970/71 Pyper [45] thoroughly worked out the symmetry properties that can profitably be used in the irreducible Liouville approach, which is based on transition frequencies, but not in the conventional Hamilton approach, which is based on energies. The Liouville approach is sometimes called the direct method [46], and operators in Liouville space
are often called superoperators. Spin relaxation in irreducible representation for arbitrary ranks \( L \) was treated in 1969 by Gabriel [47] in the context of nuclear physics (PAC), and independently in 1970 by Happer [48] in the context of atomic physics (optical pumping). The use of superoperators in NMR and spin relaxation was reviewed in 1982 by Jeener [49]. The theory was further worked out for pulse NMR by Bain, as reviewed in [50], and by Sanctuary for general NMR, both for free single spins [51] and a multitude of coupled spins [52]. Alternative approaches to the irreducible tensor method in NMR include the fictitious spin-½ method [53], quaternions [54], and Floquet theory [55].

In more recent times, Goldmann [56] reviewed spin-lattice relaxation in a representation-free manner, and Nielsen and Robinson [57] reviewed Redfield’s relaxation theory in terms of irreducible tensor operators. Van Beek et al [58] succeeded in experimentally separating each component \( \rho_{LM} \) of the irreducible density matrix by appropriate NMR pulse sequences (a procedure called quantum state tomography [59] in the context of quantum computing). Bain [60] recently gave an elementary introduction to spherical tensors in NMR, including an extensive list of references. Quadrupole interactions in solid-state NMR were reviewed in [61].

4. Derivation of the spin precession term

We now come to the central part of this paper, the derivation of the generalized precession equations from a small number of elementary steps. Relaxation effects will be discussed in section 5.

For our more detailed discussion, we first recall the definition of an irreducible tensor operator via its commutation relations with the elements \( L_z \) and \( L_\pm \) of the orbital angular momentum operator \( [8, 9, 22] \)

\[
\begin{align*}
\left[ L_z, T_{LM} \right] &= MT_{LM}, \\
\left[ L_\pm, T_{LM} \right] &= \sqrt{L(L+1) - M(M \pm 1)} T_{L,M \pm 1}.
\end{align*}
\]

The close similarity between this definition of the tensor operators \( T_{LM} \) and the well known relations for the particles’ orbital angular momentum eigenstates \( |lm\rangle \),

\[
\begin{align*}
L_z |lm\rangle &= m |lm\rangle, \\
L_\pm |lm\rangle &= \sqrt{l(l+1) - m(m \pm 1)} |l, m \pm 1\rangle,
\end{align*}
\]

can be made even more suggestive by introducing a special notation for the tensor operators. We define the tensor bras and kets (using round brackets)

\[
\begin{align*}
|LM\rangle &= T_{LM}, \\
\langle LM| &= T_{LM}^\dagger.
\end{align*}
\]

see also the discussion of the Liouville representation in the appendix of [47] and in [49]. At the same time, we assume that an operator \( A \) acts on the tensor bras and kets as
With these definitions, equations (21) and (22) become identical even with respect to notation. One only has to replace the bras and kets in equation (22) by the corresponding tensor bras and kets, i.e. equation (24) with $A = L_z$, $L_\pm$, to recover equation (22) for the tensor operators.

We then define the tensor matrix element of an operator $A$ as

$$A|LM\rangle = [A, T_{LM}],$$

$$\langle LM|A = [T_{LM}^\dagger, A].$$

(24)

The matrix elements of the product $AB$ of two operators $A$ and $B$ follow from the completeness relation for the irreducible tensor operators as

$$\langle LM'|AB|LM\rangle = \sum_{LM} \langle LM'|A|LM\rangle \langle LM|B|LM\rangle,$$

(26)

as can be seen by writing down all the matrix elements from equation (25) explicitly, where the application of the product $AB$ on $|LM\rangle$ does not mean $[AB, T_{LM}]$, but has to be interpreted as the successive operation

$$AB|LM\rangle = [A, [B, T_{LM}]].$$

(27)

as shown in equations (19.35–36) of [14].

The $T_{LM}$ are orthogonal with respect to the trace operation,

$$\text{Tr}(T_{LM}^\dagger T_{LM}') = \text{Tr}\left|\delta_{LM}\delta_{LM'}\right|^2,$$

(28)

where $\text{Tr}|T_L|^2$ is independent of $M$, as is indicated by the notation. The proof follows exactly the same line as the corresponding proof for the orthogonality of the eigenfunctions $|lm\rangle$, which can be found in any relevant textbook. Throughout this paper we assume that the $T_{LM}$ are normalized, $\text{Tr}|T_L|^2 = 1$.

The $T_{LM}$ form a complete set of orthonormal operators, and their matrix elements in the $|lm\rangle$ basis are easily calculated by means of the Wigner–Eckart theorem [8, 9, 22]

$$\langle j'm'|T_{LM}|jm\rangle = \frac{1}{\sqrt{2j + 1}} \langle j||T_L||j'\rangle \langle jmLM|j'm'\rangle,$$

(29)

with the reduced matrix element

$$\langle j||T_L||j'\rangle = \sqrt{2L + 1}$$

(30)

as an immediate consequence of the orthogonality relation for the Clebsch–Gordan coefficients; for details see appendices (A.1) and (A.2) of [14].

We are now prepared to derive the generalized spin-precession equation (4) from the Liouville equation (17). To this end we expand the density operator in terms of normalized irreducible tensor operators, [8, 9, 22]
\[ \rho = \sum_{LM} \rho_{LM} T_{LM}^\dagger. \]  

(31)

We invert this equation by multiplying both sides by \( T_{LM} \), taking the trace, and using the orthogonality of the tensor operators, and obtain

\[ \rho_{LM} = \text{Tr} \left( \rho T_{LM} \right) = \langle T_{LM} \rangle, \]

(32)

where the second equality follows the usual definition of an expectation value in terms of the density operator. When we take the trace over the basis states \( |jm \rangle \) and insert equations (29) and (30), we are back to the previous definition (18) of the state multipoles.

Hence the statistical tensors \( \rho_{LM} \) are nothing but the expectation values of the normalized irreducible tensors \( T_{LM} \), and the latter are well obtained from equations (A.1)–(A.4) by simply dropping the angular brackets therein. For a table of the \( T_{LM} \) up to \( L = 4 \), see [62] or page 227 in [9]. We then take the time derivative on both sides of equation (32), insert the Liouville equation (17) and subsequently equation (31) on the right hand side, and obtain

\[
\dot{\rho}_{LM} = \text{Tr} \left( \rho \dot{T}_{LM} \right) = i \text{Tr} \left( \left[ \rho, H \right] T_{LM} \right) = i \sum_{L_{1}M_{1}} \rho_{L_{1}M_{1}} \text{Tr} \left( \left[ T_{L_{1}M_{1}}^\dagger, H \right] T_{LM} \right).
\]

(33)

With the bracket notation (25) for the tensor matrix elements, we can write this simply as

\[
\dot{\rho}_{LM} = i \sum_{L_{1}M_{1}} \rho_{L_{1}M_{1}} \left( L_{2} M_{2} | H | LM \right).
\]

(34)

We then also expand the Hamiltonian \( H \) in terms of normalized irreducible tensor operators,

\[ H = \sum_{L,M} \Omega_{L,M} T_{L,M}^\dagger. \]

(35)

Inserting this into equation (34) gives

\[
\dot{\rho}_{LM} = i \sum_{L_{1}M_{1}L_{2}M_{2}} \Omega_{L_{1}M_{1}} \rho_{L_{1}M_{1}} \left( L_{2} M_{2} | T_{L_{1}M_{1}}^\dagger | LM \right).
\]

(36)

Next we have to evaluate the tensor matrix elements \( \left( L_{2} M_{2} | T_{L_{1}M_{1}}^\dagger | LM \right) = \left( LM | T_{L_{1}M_{1}} | L_{2} M_{2} \right)^* \) with round brackets. Because of the one-to-one correspondence of equations (21) and (22), each proof for the tensor functions is automatically true for the tensor operators, and vice versa. In particular, we can directly apply the Wigner–Eckart theorem to calculate the matrix elements with round tensor bra–kets [45, 52]

\[
\left( LM | T_{L_{1}M_{1}} | L_{2} M_{2} \right) = \frac{1}{\sqrt{2L + 1}} \left( L_{i} | T_{L_{i}} | L_{2} \right) \left( L_{2} M_{2} | L_{1} M_{1} | LM \right).
\]

(37)

Inserting this into equation (36), we immediately arrive at the generalized spin precession equation (4) with coefficients

\[
c_{j} \left( L_{1} L_{2} L \right) = -\frac{1}{\sqrt{2L + 1}} \left( L_{i} | T_{L_{i}} | L_{2} \right).
\]

(38)
Hence, by a consequent use of the normalized irreducible tensors and the round-bracket
tensor matrix elements, the derivation of the generalized spin precession equation (4) has been
reduced to a small number of elementary steps. The huge progress becomes evident if one
compares the present calculation with the one in Fano’s original paper [7]. Only the
Wigner–Eckart theorem has been used in the derivation. Since this is a universal theorem
holding in all symmetry groups, the generalized spin precession equation is also applicable in
all groups. The individual group structures only enter in the calculation of the reduced matrix
element in equation (38). It is only here where some computational effort is needed; see appendix (A.3)
of [14]. If this is done, one obtains
\[
\begin{bmatrix}
L_1 & L_2 & L
\end{bmatrix}
\begin{bmatrix}
L_1 \ L_2 \ L
\end{bmatrix}
\begin{bmatrix}
-1 -1
\end{bmatrix}
\begin{bmatrix}
\sqrt{(2L_1 + 1)(2L_2 + 1)(2L + 1)}
\end{bmatrix}
\begin{bmatrix}
L_1 + L_2 - L
\end{bmatrix}
\begin{bmatrix}
L
\end{bmatrix}
\]
with a Wigner 6j symbol in curly brackets, in accordance with Fano’s equation (7) in [7].

5. Derivation of the relaxation term

Let us now turn to the discussion of the relaxation term in equation (6). In relaxation studies, the
tensor bra–ket notation (23) to (25) exhibits its full power. There is usually a system
Hamiltonian \(H_S\) that is under the control of the experimentalist; the environment is described by
a bath Hamiltonian \(H_B\), which cannot normally be controlled; a Hamiltonian \(H_{SB}\) then couples
the system to the environment. Removing the bath Hamiltonian \(H_B\) by a standard
transformation (see [12, 45], or for more details appendix (A.9) of [14]), one obtains an
effective Hamiltonian \(H = H_S + H_{SB}(t)\), where the coupling Hamiltonian
\[
H_{SB}(t) = e^{iH_B}H_{SB}(0)e^{-iH_B}
\]
has now turned into a time-dependent interaction. After another transformation
\[
\tilde{\rho} = e^{iH_B}\rho e^{-iH_B}
\]
we arrive at the Liouville equation in the interaction representation,
\[
\hat{\rho}_{LM} = i \sum_{LM'} \hat{H}_{LM}(t)|LM\rangle\langle LM'|,
\]
obtained from equation (34) by replacing \(\rho\) by \(\tilde{\rho}\) and \(H\) with
\[
\hat{H}_{LM}(t) = e^{iH_B}H_{SB}(t)e^{-iH_B}.
\]

It is beyond the scope of this paper to go into the details of relaxation theory. Instead we
simply follow the standard approach [44, 49] and treat the relaxation in second-order
perturbation theory. To this end we integrate both sides of equation (42) over \(t\),
\[
\tilde{\rho}_{LM}(t) = \tilde{\rho}_{LM}(0) + i \sum_{LM'} \int_0^t d\tau \tilde{\rho}_{L'M'}(\tau) \langle L'M'|\hat{H}_{LM}(\tau)|LM\rangle,
\]
where we relabel the indices, and substitute this expression for \(\tilde{\rho}_{LM}(t)\) on the right hand side of
equation (42) to obtain
\[ \hat{\rho}_{LM}(t) = i \sum_{L'M'} \tilde{\rho}_{LM'}(0) \left( L'M' | \tilde{H}_1(t) | LM \right) \\
- \sum_{L'M'} \int_0^t d\tau \, \tilde{\rho}_{LM'}(\tau) \left( L'M' | \tilde{H}_1(\tau) | LM' \right) \left( L'M' | \tilde{H}_1(t) | LM \right) \\
= i \sum_{LM} \tilde{\rho}_{LM}(0) \left( L'M' | \tilde{H}_1(t) | LM \right) \\
- \sum_{L'M'} \int_0^t d\tau \, \tilde{\rho}_{LM'}(t-\tau) \left( L'M' | \tilde{H}_1(t-\tau) \hat{H}_1(t) | LM \right), \tag{45} \]

where in the second step the completeness of the irreducible tensor operators has been used. In addition, we changed the integration variable from \( \tau \) to \( t-\tau \). To avoid a possible misinterpretation of the equation, we recall the operator multiplication convention (27).

Equation (45) is still exact, but to proceed further we have to apply the following approximations, as used by \([44, 49]\) in the ‘extreme narrowing’ approach.

(i) First we assume that \( \tilde{H}_1(t) \) varies rapidly with time as compared to \( \tilde{\rho}_{LM}(t) \), so we can replace \( \tilde{H}_1(t) \) and \( \tilde{H}_1(t-\tau) \hat{H}_1(t) \) by their time averages over these rapid fluctuations.

(ii) Without loss of generality we may assume that the time average \( \tilde{H}_1(t) \) disappears, if needed, after a proper redefinition of the system Hamiltonian \( H_S \).

(iii) Next, the correlation function \( \tilde{H}_1(t-\tau) \tilde{H}_1(t) \) will typically decay on a time scale \( \tau_c \), which is the correlation time for the fluctuations of the bath variables. If \( \tau_c \) is short compared to the time scale where the changes in \( \tilde{\rho}_{LM}(t) \) take place, we may replace \( t-\tau \) in the argument of \( \tilde{\rho}_{LM} \) on the right hand side by \( t \), and extend the upper limit of the integration to infinity.

(iv) Finally, in second-order perturbation theory we restrict the sum over \( L',M' \) to just one term \( L,M \).

We then obtain
\[ \hat{\rho}_{LM} = -\tilde{\rho}_{LM}/\tau_{LM}, \tag{46} \]

where
\[ \frac{1}{\tau_{LM}} = \int_0^\infty d\tau \left( LM | \tilde{H}_1(t-\tau) \tilde{H}_1(t) | LM \right), \tag{47} \]

see also equation (20) of [63], and section 5.2 therein, for an equivalent expression but in terms of angular momentum matrix elements.

Going back to the laboratory frame by inverting transformation (41), we obtain the generalized spin precession equation including the relaxation term. We see that on the level of the applied approximations, each tensor component \( \rho_{LM} \) decays exponentially with its own decay constant \( \tau_{LM} \), but this is no longer true for more evolved relaxation theories, in particular if fluctuating quadrupole interactions are involved [48]. The decay towards a thermal equilibrium is not obtained in this way, but this deficiency can be repaired by taking into account the Boltzmann polarization of the bath. To get explicit expressions for the relaxation rates from equation (47) for various situations found in the experiments, some effort is still needed [12].

Again, since nothing but the Wigner–Eckart theorem (37) was used in the derivation, the generalized Bloch equation (4) (under the approximations made above) is valid for arbitrary
groups. The individual group structures enter only in the calculation of reduced matrix elements (39), and in the explicit evaluation of the relaxation rates from equation (47).

6. Conclusions

The generalized Bloch equations (6) give a very pictorial visualization of the complicated interactions of a spin ensemble exposed to external multipole fields, in the same way as the original Bloch equations do for purely magnetic interactions. We showed a number of typical applications of these equations in atomic, nuclear and condensed matter physics. Using a special bra–ket notation, the derivation of the generalized Bloch precession equations from the Liouville equation has been reduced to a small number of simple steps, both for the spin precession term and the relaxation term.

Appendix

We first give the elements of the statistical tensors \( \rho_{L_1} \) and of the frequency tensors \( \Omega_{L_1} \) for ranks \( L_1, L_2 \leq 2 \), as again derived from first principles in \([14]\). We then give the coefficients \( c_j(L_1L_2L) \) for ranks \( L_1 \leq 2 \) and for arbitrary \( j, L, L_2 \). Then we list the elements of the Liouville matrix \( \hat{L} \) for \( j = 1 \).

The vector polarization \( \rho_1 \) is linked to \( P \) in equation (3) as

\[
\rho_{10} = a_1 \langle J_z \rangle = a_1 p_z,
\]

\[
\rho_{11} = \mp \sqrt{1/2} a_1 \langle J_z \rangle = \mp \sqrt{1/2} a_1 (p_z \pm i p_y),
\]

with

\[
a_1 = \left[ 3/j (j + 1) (2j + 1) \right]^{1/2}.
\]

The alignment \( \rho_2 \) is defined by its components

\[
\rho_{20} = a_2 \left[ 3 \langle j_z^2 \rangle - j (j + 1) \right],
\]

\[
\rho_{21} = \mp \sqrt{3/2} a_2 \langle j_z j_x \pm j j_z \rangle,
\]

\[
\rho_{22} = \sqrt{3/2} a_2 \langle j_x^2 \rangle,
\]

with

\[
a_2 = \left[ 20/(2j - 1) 2j (2j + 1) (2j + 2) (2j + 3) \right]^{1/2}.
\]

The interaction frequencies are, for the usually dominating magnetic dipole and electric quadrupole interactions,
\[
\Omega_{10} = \frac{\gamma B_z}{a_1}, \quad \Omega_{1\pm 1} = \mp \frac{\gamma \left( B_z \pm iB_y \right)}{\sqrt{2} a_1},
\]
\[
\Omega_{20} = \frac{\omega_Q}{a_2}, \quad \Omega_{2\pm 1} = \mp \frac{\omega_Q}{\sqrt{6} a_2} \left( \frac{\varphi_{xx} \pm i\varphi_{xy}}{\varphi_{zz}} \right),
\]
\[
\Omega_{2\pm 2} = \frac{\omega_Q}{\sqrt{6} a_2} \left( \frac{\varphi_{xx} - \varphi_{yz} \pm 2i\varphi_{xzy}}{\varphi_{zz}} \right),
\]
(A.5)

with the quadrupole interaction frequency \[61, 64\]
\[
\omega_Q = \frac{e^2 \varphi_{xx}}{4j(2j - 1)} ,
\]
(A.6)

where \(eQ\) is the quadrupole moment of the particles, and with the second spatial derivatives of the external electric potential \(\varphi\), which constitute the elements of the electric field gradient tensor. In principal axes representation, with the asymmetry parameter
\[
\eta = \frac{\varphi_{xx} - \varphi_{xzy}}{\varphi_{zz}} ,
\]
(A.7)

we have \(\Omega_{2\pm 1} = 0\) and \(\Omega_{2\pm 2} = \sqrt{1/6} \eta \omega_Q / a_2\).

The only non-vanishing coefficients \(c_j(L_1L_2L)\) for \(L_1 = 1, 2\), corresponding to magnetic dipole and electric quadrupole interactions, respectively, are from equations (38) and (39),
\[
c_j(1LL) = -a_1\sqrt{L(L + 1)},
\]
(A.8)
\[
c_j(2, L, L - 1) = -a_2\sqrt{3(2j + L + 1)(2j - L + 1)(L - 1)L(L + 1)/(2L + 1)}
\]
\[
= -c_j(2, L - 1, L).
\]
(A.9)

The diagonal submatrices \(\mathbf{\hat{L}}_{11}, \mathbf{\hat{L}}_{22}\) of the Liouville matrix \(\mathbf{\hat{L}}\) are independent of \(j\). They read, starting with the \(M = M' = +L\) element in the upper left, and with the abbreviations
\(a = \sqrt{1/2}, b = \sqrt{2}, c = \sqrt{3/2}\),
\[
\mathbf{\hat{L}}_{11} = \begin{pmatrix}
-\Omega_{10} & a\Omega_{11} & 0 \\
0 & a\Omega_{11}^* & 0 \\
0 & 0 & a\Omega_{11}^* \\
0 & 0 & \Omega_{10}
\end{pmatrix},
\]
(A.10)
\[
\mathbf{\hat{L}}_{22} = \begin{pmatrix}
-b\Omega_{10} & \Omega_{11} & 0 & 0 & 0 \\
\Omega_{11}^* & -a\Omega_{10} & c\Omega_{11} & 0 & 0 \\
0 & c\Omega_{11}^* & 0 & c\Omega_{41} & 0 \\
0 & 0 & c\Omega_{41}^* & a\Omega_{10} & \Omega_{11} \\
0 & 0 & 0 & \Omega_{10}^* & b\Omega_{10}
\end{pmatrix},
\]
(A.11)
The off-diagonal submatrices are, for \( j = 1 \),

\[
\hat{L}_{12} = \hat{L}_{21}^\dagger = \begin{pmatrix}
-\Omega_{21}^* & -c\Omega_{20} & c\Omega_{21} & -h\Omega_{22}^* \\
 b\Omega_{22}^* & a\Omega_{21}^* & 0 & -b\Omega_{22} \\
 0 & \Omega_{22}^* & c\Omega_{21} & -\Omega_{22}^* \\
 c\Omega_{20} & c\Omega_{21} & c\Omega_{22} & -\Omega_{21}
\end{pmatrix}.
\]

(A.12)

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