Published in final edited form as:

J Magn Reson. 2013 August ; 233: 80–86. doi:10.1016/j.jmr.2013.05.009.

Bloch Equations for Anisotropic Paramagnetic Centers with Spin of $\frac{1}{2}$

Alexander G. Maryasov^a and Michael K. Bowman^{*,b}

^aThe V.V.Voevodsky Institute of Chemical Kinetics and Combustion, The Siberian Branch of the Russian Academy of Science, 3 Institutskaya St., Novosibirsk 630090, Russia.

^b Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, AL 35487-0336, USA.

Abstract

The Bloch equations are an invaluable tool in magnetic resonance for describing the dynamics of isotropic spin systems. However, when the Bloch equations are reformulated for anisotropic spin systems, much of their utility is lost because the spin evolution they describe is not physically observable. A set of Bloch-like equations are derived for these anisotropic systems in terms of the magnetic moment which is the physical property measured in magnetic resonance and other experiments. The equations describe the dynamics of the magnetic moment including relaxation and only contain parameters that are experimentally measurable.

Keywords

Bloch Equations; EPR; Anisotropic g tensor

Introduction

The Bloch equations [1] describe the dynamics and relaxation of the magnetic moment of a sample caused by paramagnetic centers (PCs) interacting with external magnetic fields. The equations were introduced first as a phenomenological description but later were shown to be exact for non-interacting PCs having spins of $\frac{1}{2}$ [2]. The important restriction in the quantum mechanical derivation was that the magnetic moment and spin vector of the PC must be collinear. This is a good approximation for PCs with isotropic g -tensors, such as organic radicals, but fails for many PCs containing paramagnetic metal ions. The magnetic moment and the spin vector are related to each other through the g -tensor, so that g -anisotropy produces a magnetic moment that is generally not collinear with the spin vector.

Bloch-like equations can be written for the behaviour of spins, or indeed any two-level quantum mechanical system. Such equations, analogous to the Maxwell-Bloch or optical Bloch equations, lack one of the beautiful and most useful features of the Bloch equations. They do not describe a physically-observable property of the system. Rather they describe

© 2013 Elsevier Inc. All rights reserved.

*mkbowman@as.ua.edu phone: +1-205-348-7846 fax: +1-205-348-9104. A. G. Maryasov maryasov@kinetics.nsc.ru.

Publisher's Disclaimer: This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final citable form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

the evolution of spin states that do not have an associated physical observable and whose behaviour can only be deduced from indirect measurements.

The distinction between spin and magnetic moment may seem to be very subtle. But it becomes quite important when trying to understand or manipulate magnetic interactions of biological PCs with other PCs or with nuclear spins [3, 4]; when considering the magnetic properties of a material; or when planning or interpreting magnetic resonance measurements. Here we extend the Bloch equations to describe the observable magnetic moments of anisotropic PCs. These equations differ significantly from the case for isotropic PCs and describe the evolution and relaxation of the magnetic moment. Yet, the equations converge to the classic Bloch equations as the g -anisotropy vanishes. They are readily extensible to any observable of a two-level quantum mechanical system that is related to the density matrix through a second-rank pseudo-tensor analogous to the g -factor.

Bloch Equations

Isotropic PCs

The classic form of the Bloch equations for evolution of the system magnetic moment vector, $\vec{M}(t)$, in an external magnetic field, $\vec{B}(t)$, is [1]

$$\frac{\partial}{\partial t} \vec{M}(t) = \frac{g\beta}{\hbar} \vec{M}(t) \times \vec{B}(t) - \overleftrightarrow{R} \left(\vec{M}(t) - \vec{M}_{eq} \right) \quad (1)$$

where g is the g -factor of the PC (g may be positive or negative), β is the Bohr magneton (some authors consider β negative for electrons, which we will follow to have the same equations as for protons in NMR), $\hbar$ is Planck's constant, $\overleftrightarrow{R}$ is the relaxation operator, and $\vec{M}_{eq}$ is the equilibrium value of the magnetic moment. The external magnetic field in magnetic resonance is typically the sum of a constant part and an oscillating (microwave, mw) part, $\vec{B}(t) = \vec{B}_0 + 2\vec{B}_1 \cos(\omega t + \varphi)$, with B the strength of the oscillating field, whereas ω and φ are its frequency and phase, respectively. The equilibrium value of the magnetic moment is defined in the absence of mw irradiation. To describe the evolution of the magnetic moment, a laboratory frame is defined with its z axis along $\vec{B}_0$, and the x axis along the linearly-polarized mw field $\vec{B}_1$ (typically these two fields are perpendicular, which we assume). The y axis is chosen to provide a right-handed coordinate system. The unit vectors along the x , y , and z axes are $\vec{x}$, $\vec{y}$, and $\vec{z}$ respectively.

In this lab frame, the relaxation term is written as

$$\overleftrightarrow{R} \left(\vec{M}(t) - \vec{M}_{eq} \right) = \frac{1}{T_2} (M_x \vec{x} + M_y \vec{y}) + \frac{1}{T_1} (M_z - M_{eq}) \vec{z} \quad (2)$$

M_q is the projection of the magnetic moment vector onto the q axis ($q = x, y, z$), T_1 and T_2 are longitudinal (or spin-lattice) and transverse (or phase) relaxation times. The vector $\vec{M}_{eq}$ is directed along the z axis and has length M_{eq} (its exact value is given below when considering anisotropic PCs). When the relaxation times are very long so that it is possible to neglect relaxation during the observation, the length of the magnetic moment does not vary (see, e.g., [2]), and it is possible to show

$$\frac{d}{dt} |\vec{M}(t)|^2 = 2 \frac{g\beta}{\hbar} \vec{M}^T(t) \left\{ \vec{M}(t) \times \vec{B}(t) \right\} = 0 \quad (3)$$

where the superscript^T denotes the vector or matrix transpose. The evolution of the magnetic moment in this limiting case is just the precession of the magnetic moment around the instantaneous direction of the external magnetic field at the instantaneous Zeeman frequency $\omega_z = |g\beta \vec{B}(t)|/\hbar$, in a clockwise or counter clockwise direction depending on the sign of the g -factor. The first term on the right hand side of Eq. (1) was well known from electrodynamics and Bloch added the relaxation term given in Eq. (2) to describe the return of the system to equilibrium.

Quantum mechanical formulation

The state of a system having real or effective spin of $1/2$ (or any two-level system) is described by its density operator ρ which may be represented as a linear combination of spin matrices

$$\rho = 2\vec{s}^T \cdot \hat{\vec{S}} \quad (4)$$

where $\vec{s}$ is the PC spin vector and $\hat{\vec{S}}$ is the vector spin operator.

$$\vec{s} = \text{Tr} \left(\rho \hat{\vec{S}} \right) \quad (5)$$

The evolution of any system with spin of $1/2$ may be completely described with this time-dependent vector and any two-level system is described by the analogous vector in the Maxwell-Bloch equations.

The evolution of ρ obeys the equation

$$\frac{\partial}{\partial t} \rho(t) = \frac{i}{\hbar} \{ \rho(t) \hat{H} - \hat{H} \rho(t) \} \quad (6)$$

here $\hat{H}$ is the system Hamiltonian which may be time-dependent, *e.g.*, when a mw magnetic field is applied in a spectroscopic measurement. For PCs with spin $S = 1/2$ the spin Hamiltonian is

$$\hat{H} = -\vec{B}^T \cdot \hat{\vec{\mu}} \quad (7)$$

where $\hat{\vec{\mu}}$ is the magnetic moment operator and $\vec{B}$ may be expanded to include hyperfine, dipolar and similar fields. In the isotropic case, $\hat{\vec{\mu}} = g\beta \hat{\vec{S}}$, but for anisotropic PC

$$\hat{\vec{\mu}} = \beta \overleftrightarrow{g} \cdot \hat{\vec{S}} \quad (8)$$

where $\overleftrightarrow{g}$ denotes the so-called g tensor or, more exactly, g matrix, which is a 3×3 matrix. The properties of the g tensor are detailed by Abragam and Bleaney [5]. The magnetic moment vector, $\vec{M}$, is

$$\vec{M} = \text{Tr} \left(\rho \hat{\vec{\mu}} \right) \quad (9)$$

giving, with Eqs. (4) and (8)

$$\vec{M} = \beta \overleftrightarrow{g} \vec{S} \quad (10)$$

For isotropic PCs, $\vec{M}$ and $\vec{S}$ are collinear; but in the anisotropic case, these vectors generally point in different directions.

The first term on the right hand side of Eq. (1) may be easily obtained in the isotropic case after substitution of $\vec{S} = \vec{M}/g\beta$ into Eq. (4), use of Eqs. (7-9) and the properties of spin operators [6].

When there is g tensor anisotropy, the respective operations become more complicated. It is much easier to obtain the equation of motion for the spin vector and then apply Eq. (10) to obtain equations for the motion of the magnetic moment. To do this, let us write the spin Hamiltonian (7-8)

$$\hat{H} = -\beta \vec{B}_{eff}^T \hat{\vec{S}} \quad (11)$$

where the effective magnetic field is introduced as

$$\vec{B}_{eff} = \overleftrightarrow{g}^T \vec{B} \quad (12)$$

Eqs. (11-12) differ from the usual definition by the omission of g_e and was adopted to simplify subsequent equations and because B_{eff} does not appear in the final equations. Substitution of Eqs. (4) and (11) into (6) is followed by the calculations used to derive the isotropic Bloch equations in [2], with the relation in Eq.(3.39) from [6],

$\left(\vec{a}^T \hat{\vec{S}} \right) \hat{\vec{S}} - \hat{\vec{S}} \left(\vec{a}^T \hat{\vec{S}} \right) = -i \vec{a} \times \hat{\vec{S}}$ where $\vec{a}$ is an arbitrary vector that commutes with the spin operators. This results in the dynamic term of the Bloch equations for the spin vector $\vec{S}$ in the case of anisotropic g tensor,

$$\frac{\partial}{\partial t} \vec{S}(t) = \frac{\beta}{\hbar} \vec{S}(t) \times \vec{B}_{eff}(t) \quad (13)$$

It is possible to derive the relaxation term after some reasonable assumptions about the spin-lattice relaxation processes. The standard approach is to introduce a rapidly fluctuating term [2, 7] in the spin Hamiltonian as

$$\hat{H} = -\beta \vec{B}_{eff}^T \hat{\vec{S}} + \vec{F}^T(t) \hat{\vec{S}} \quad (14)$$

When the lattice variable $\vec{F}(t)$ obeys simple conditions listed by Redfield [8] and Wangness and Bloch [9], it is possible to write Eq. (13) as

$$\frac{\partial}{\partial t} \vec{S}(t) = \frac{\beta}{\hbar} \vec{S}(t) \times \vec{B}_{eff}(t) - \frac{1}{T_2} \vec{S}_\perp - \frac{1}{T_1} (\vec{S}_\parallel - \vec{S}_{eq}) \quad (15)$$

Here $\vec{S}_{eq}$ is the equilibrium value of the spin vector. It is directed along the effective magnetic field direction, with $\vec{S}_\perp$ and $\vec{S}_\parallel$ being components of the spin vector perpendicular and parallel to the effective field direction, respectively. The equilibrium spin vector is [2]

$$\vec{S}_{eq} = \frac{\text{Tr}\left(\vec{S} \exp\left(\frac{\beta \vec{B}_{eff}^T \vec{S}}{kT}\right)\right)}{\text{Tr}\left(\exp\left(\frac{\beta \vec{B}_{eff}^T \vec{S}}{kT}\right)\right)} \quad (16)$$

and, for spin 1/2, reduces to

$$\vec{S}_{eq} = \frac{\vec{B}_{eff}}{2B_{eff}} \tanh\left(\frac{\beta B_{eff}}{2kT}\right) \quad (17)$$

where B_{eff} is the length of the vector $\vec{B}_{eff}$. In the high-temperature limit when the Zeeman energy is much less than thermal energy, Eq. (17) becomes

$$\vec{S}_{eq} = \frac{\beta}{4kT} \vec{B}_{eff} \quad (18)$$

In principle, Eqs. (15) and (17) provide a complete description of the spin dynamics. The fundamental issue motivating this paper is that the spin vector is impossible to measure in any magnetic resonance experiment. In most physical measurements (including, *e.g.*, a magnetic balance), the measurable quantity or observable is the magnetic moment, not the spin. The relation between $\vec{M}$ and $\vec{S}$ in Eq. (10) appears to give a trivial resolution of the issue. The most direct approach would be to calculate the evolution of $\vec{S}$ using Eqs. (12) and (15), from the initial system state, Eq. (17), and then obtain $\vec{M}$ using the g tensor and Eq. (10). This approach was followed in our previous paper [3] and the spin dynamics of a PC with anisotropic g -tensor was examined in the absence of relaxation for several types of pulsed EPR experiments.

Yet, this approach is not as satisfactory as it first seems because the g tensor itself is not measurable, see [5] for details. It is possible to obtain only two quantities from magnetic resonance experiments: the g tensor signature, or sign of the g tensor determinant, σ ,

$$\sigma = \text{sign}\left(\text{Det}\left(\overleftrightarrow{g}\right)\right) \quad (19)$$

(which was confusingly called s in [3]) and the symmetric tensor $\overleftrightarrow{G}$, which is the convolution of the g tensor over spin indices,

$$\overleftrightarrow{G} = \overleftrightarrow{g} \quad \overleftrightarrow{g}^T \quad (20)$$

The signature σ tells the direction of rotation of the magnetic moment vector around the external magnetic field. The components of the tensor $\overleftrightarrow{G}$ and their combinations define all observable properties such as the Zeeman frequency, ω_0 , and the transition probability, p , between electron spin states for weak mw irradiation at ω with the applied linearly-polarized magnetic field $\vec{B}_1 = 2B_1 \vec{x} \cos(\omega t)$ perpendicular to $\vec{B}_0 = B_0 \vec{z}$, so that [5]

$$\omega_0 = \frac{|\beta \vec{B}_{eff}|}{\hbar} = \frac{|\beta|}{\hbar} g_{eff} B_0 \quad (21)$$

$$p \propto g_1^2 B_1^2 \quad (22)$$

where g_{eff} is the effective value of the g tensor,

$$g_{eff} = \sqrt{\vec{z}^T \overleftrightarrow{G} \vec{z}} = \sqrt{G_{zz}} \quad (23)$$

$$\begin{aligned} g_1 &= \sqrt{\vec{x}^T \overleftrightarrow{G} \vec{x} - \frac{(\vec{x}^T \overleftrightarrow{G} \vec{z})^2}{(\vec{z}^T \overleftrightarrow{G} \vec{z})}} \\ &= \sqrt{G_{xx} - \frac{G_{xz}^2}{G_{zz}}} \end{aligned} \quad (24)$$

and the indices x, y, z refer to the lab frame. Although there are various standards and proposals for extracting the g tensor from s and $\overleftrightarrow{G}$, they impose arbitrary restrictions on g or require more information than is routinely available. For instance, most commercial EPR spectrometers are inherently incapable of measuring σ ; and EPR studies are often made before the molecular structure is known in sufficient detail for other approaches, *e.g.* [10]. Even worse, there is no generally accepted convention for extracting a g tensor from a $\overleftrightarrow{G}$. Several different, equally-likely g tensors can be obtained from one $\overleftrightarrow{G}$.

Equations for magnetic moment

In view of this difficulty with the g tensor for an anisotropic spin system, we have developed Bloch equations in closed form for the physical observable, the magnetic moment vector. Starting from Eq. (15) and making use of Eq. (10), the very first step is to calculate the equilibrium magnetic moment vector, $\vec{M}_{eq}$, combining Eqs. (10), (17), (20) and (21)

$$\vec{M}_{eq} = \frac{|\beta| \overleftrightarrow{G} \vec{B}_0}{2 g_{eff} B_0} \tanh\left(\frac{\hbar \omega_0}{2 kT}\right) = \frac{|\beta|}{2 g_{eff}} \overleftrightarrow{G} \vec{z} \tanh\left(\frac{\hbar \omega_0}{2 kT}\right) \quad (25)$$

In the high-temperature limit, this reduces to

$$\vec{M}_{eq} \approx \frac{\beta^2}{4 kT} \overleftrightarrow{G} \vec{B}_0 \quad (26)$$

The $\overleftrightarrow{G} \vec{z}$ term in Eq. (25) means that $\vec{M}_{eq}$ has transverse components in the lab frame in the general case. $\vec{M}_{eq}$ is parallel to the external magnetic field only when the field $\vec{B}_0$ is directed along one of the principal axes of $\overleftrightarrow{G}$.

The dynamics of $\vec{M}$ can be obtained from Eq. (15), in the limit of negligible relaxation by multiplying both sides by $\beta \overleftrightarrow{g}$ and an arbitrary non-zero vector $\vec{a}^T$, making the substitution

$$\vec{s} = (\beta \overleftrightarrow{g})^{-1} \vec{M} \quad (27)$$

which is possible when the g tensor has non-zero determinant, that is, $\sigma \neq 0$. This results in

$$\begin{aligned}
\vec{a}^T \frac{\partial}{\partial t} \vec{M}(t) &= \frac{\beta}{\hbar} \vec{a}^T \left\{ \vec{g}^{-1} \vec{M}(t) \times \vec{g}^T \vec{B} \right\} \\
&= \frac{\beta}{\hbar} \left(\vec{g}^T \vec{a} \right)^T \left\{ \vec{g}^T \left(\left(\vec{g}^T \right)^{-1} \vec{g}^{-1} \vec{M}(t) \right) \times \vec{g}^T \vec{B} \right\} \quad (28) \\
&= \frac{\beta}{\hbar} \left(\vec{g}^T \vec{a} \right)^T \left\{ \vec{g}^T \left(\vec{G}^{-1} \vec{M}(t) \right) \times \vec{g}^T \vec{B} \right\}
\end{aligned}$$

because $\left(\vec{g}^T \right)^{-1} \vec{g}^{-1} = \vec{G}^{-1}$ and can be rearranged using the relationship for an arbitrary 3×3 matrix, $\vec{A}$, and 3 arbitrary vectors, $\vec{a}_i$ [11, Chapter VII B4],

$$\left(\vec{A} \vec{a}_1 \right)^T \left\{ \left(\vec{A} \vec{a}_2 \right) \times \left(\vec{A} \vec{a}_3 \right) \right\} = \text{Det} \left(\vec{A} \right) \vec{a}_1^T \left\{ \vec{a}_2 \times \vec{a}_3 \right\} \quad (29)$$

to give

$$\begin{aligned}
\vec{a}^T \frac{\partial}{\partial t} \vec{M}(t) &= \frac{\beta}{\hbar} \text{Det} \left(\vec{g}^T \right) \vec{a}^T \left\{ \left(\vec{G}^{-1} \vec{M}(t) \right) \times \vec{B} \right\} \\
\frac{\partial}{\partial t} \vec{M}(t) &= \frac{\beta}{\hbar} \text{Det} \left(\vec{g}^T \right) \left\{ \vec{G}^{-1} \vec{M}(t) \times \vec{B} \right\} \quad (30a) \\
&= \sigma \frac{\beta}{\hbar} \sqrt{\text{Det} \left(\vec{G} \right)} \left\{ \vec{G}^{-1} \vec{M}(t) \times \vec{B} \right\}
\end{aligned}$$

which only contains terms: σ , G , and M , that are measurable in a magnetic resonance experiment. In a constant magnetic field as would be the case during free precession, $\vec{B} = B_0 \vec{z}$, and Eq. (30a) becomes

$$\begin{aligned}
\frac{\partial}{\partial t} \vec{M}(t) &= \frac{\beta}{\hbar} \frac{B_0}{\hbar} \left\{ \vec{Q} \vec{M}(t) \times \vec{z} \right\} \\
&= \frac{\beta}{\hbar} \frac{B_0}{\hbar} \left(\vec{x} \left(Q_{yx} M_x + Q_{yy} M_y + Q_{yz} M_z \right) - \vec{y} \left(Q_{xx} M_x + Q_{xy} M_y + Q_{xz} M_z \right) \right) \quad (30b) \\
&= \frac{\beta}{\hbar} \frac{B_0}{\hbar} \begin{pmatrix} Q_{yx} & Q_{yy} & Q_{yz} \\ -Q_{xx} & -Q_{xy} & -Q_{xz} \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} M_x \\ M_y \\ M_z \end{pmatrix}
\end{aligned}$$

where $\vec{Q} = \sigma \sqrt{\text{Det} \left(\vec{G} \right)} \vec{G}^{-1}$. The eigenvalues and eigenvectors of Eqs. (30a-b) provide a simple connection to the familiar coherences and polarizations of magnetic resonance. Eq. (30b) has three eigenvalues: $\omega_1 = 0$, $\omega_2 = i\omega_0$, $\omega_3 = -\omega_2$, with eigenvectors

$$\begin{aligned}
\vec{M}_1 &= \vec{G}^{-1} \vec{z} = G_{xz} \vec{x} + G_{yz} \vec{y} + G_{zz} \vec{z} \\
\vec{M}_2 &= \vec{x} - c \vec{y} \\
\vec{M}_3 &= \vec{x} - c^* \vec{y} \\
c &= \{ Q_{xy} - ig_{eff} \} / Q_{yy}
\end{aligned} \quad (31)$$

The magnetization eigenvector $\vec{M}_1$ with the eigenvalue of 0 is parallel to $\vec{M}_{eq}$, Eq. (25), and does not vary with time in the absence of relaxation, that is, the polarization of this PC. The two other eigenvectors are perpendicular to $\vec{B}_0$, but not necessarily to each other. For isotropic g , the $\vec{M}_{2/3}$ become $\vec{M}_{+/-}$ and are the single-quantum coherences. The orthogonality relation for the eigenvectors is more general with $\vec{G}^{-1}$ playing the role of metric tensor in magnetic moment space

$$\vec{M}_i^+ \leftrightarrow^{-1} \vec{M}_j \propto \delta_{ij} \quad (32)$$

where δ_{ij} is the Kronecker delta and the superscript⁺ indicates the Hermitian conjugate.

The length of $\vec{M}$ is not conserved in the absence of relaxation as it is for isotropic PCs and Eq. (3) is not valid. For anisotropic PCs, an even more general property is found. For any time-varying magnetic field, including during mw pulses, the quantity $\vec{M}^2 = \vec{M}^T \leftrightarrow^{-1} \vec{M}$ is conserved in the absence of relaxation. Fig. 1 illustrates how $\vec{M}$ precesses around its equilibrium direction in a static magnetic field. The projection of $\vec{M}$ onto the external magnetic field does not vary (so that the system energy is conserved). Yet, the tip of the magnetic moment vector traces an elliptical path in a plane perpendicular to $\vec{B}_0$ so that the perpendicular components of $\vec{M}$ are elliptically polarized. If the system is initially at equilibrium in a static field, $\vec{M}^2$ may be calculated explicitly as

$$\vec{M}^2 = \vec{M}^T \leftrightarrow^{-1} \vec{M} = \frac{\beta^2 \tanh^2 \left(\frac{\hbar \omega_0}{2kT} \right)}{4g_{eff}^2} \left(\vec{z}^T \leftrightarrow \leftrightarrow^{-1} \leftrightarrow \vec{z} \right) = \frac{\beta^2}{4} \tanh^2 \left(\frac{\beta g_{eff} B_0}{2kT} \right) \quad (33)$$

which defines an elliptic surface in the lab frame. If the observation time t is much shorter than the relaxation times, $t \ll T_1, T_2$, then the tip of the magnetic moment vector always touches the elliptic surface, and its trajectory on that surface is determined by the external magnetic fields. Fig. 2 illustrates the trajectory of $\vec{M}$ during a microwave pulse, as it follows a spiral path on the elliptic surface from Eq. (33). It is interesting to note that at equilibrium, the magnetization vector points to the spot on the ellipsoid having the maximum projection onto the applied field which is the lowest energy on the ellipsoid for the Hamiltonian in Eq. (7). In the presence of relaxation, the $\vec{M}$ trajectory must lie inside the elliptical surface of Eq. (33). For isotropic PC this surface is a sphere.

The rotating frame is a very valuable aid for considering the dynamics of isotropic PCs. Making the reference frame rotate at the microwave frequency ensures that the motion of the magnetization is on the longer timescale of T_2, T_1 and $\hbar/(\beta g_1 B_1)$, rather than on the much shorter timescale of $1/\omega_z$. The magnetization follows a relatively short, slow path in the rotating frame that is simpler to visualize and understand than when viewed in the laboratory frame. The motion of the spin is quite simple in a tilted rotating frame for anisotropic g tensors and some details are shown in our previous paper [3]. Some of the convenient characteristics of the rotating frame presentation disappear when considering the magnetization of anisotropic PCs. The length of the magnetization varies at ω_z and $2\omega_z$ in the rotating frame. So some very rapid motions remain that are highly relevant to the physical properties of the sample.

An equation for $\vec{M}$ with the general form of the Bloch equations is obtained from Eq. (30) by adding relaxation terms arising from a Hamiltonian of the form of Eq. (14). Substitution of Eq. (27) into the relaxation terms of Eq. (15) gives

$$\frac{\partial}{\partial t} \vec{M}(t) = \sigma \frac{\beta}{\hbar} \sqrt{\text{Det} \left(\leftrightarrow \right)} \left\{ \leftrightarrow^{-1} \vec{M}(t) \times \vec{B} \right\} - \leftrightarrow \left(\vec{M}(t) - \vec{M}_{eq} \right) \quad (34)$$

The relaxation term turns out to be similar to Eq. (2); the difference between the magnetic moment and its equilibrium value, that is, $\vec{M}(t) - \vec{M}_{eq}$, relaxes

$$\begin{aligned}
& \overleftrightarrow{R} \left(\vec{M}(t) - \vec{M}_{eq} \right) \\
&= \vec{x} \left\{ \frac{1}{T_1} (M_{x \text{ stat}} - M_{x \text{ eq}}) + \frac{1}{T_2} (M_x - M_{x \text{ stat}}) \right\} \\
&+ \vec{y} \left\{ \frac{1}{T_1} (M_{y \text{ stat}} - M_{y \text{ eq}}) + \frac{1}{T_2} (M_y - M_{y \text{ stat}}) \right\} \\
&+ \vec{z} \left\{ \frac{1}{T_1} (M_{z \text{ stat}} - M_{z \text{ eq}}) \right\}
\end{aligned} \quad (35)$$

In Eq. (35), $\vec{M}_{stat}$ is the part of the magnetic moment that is parallel to $\vec{M}_{eq}$. Its projection along $\vec{z}$ is given by $M_{z \text{ stat}} = M_z$ and $\vec{M}_{stat} - \vec{M}_{eq}$ relaxes with a time constant T_1 . The remainder of $\vec{M}(t)$ is perpendicular to $\vec{B}_0$ and relaxes with the phase relaxation time T_2 . Eq. (35) is not a very satisfactory expression because it introduces the new vector $\vec{M}_{stat}$. However, it can be rearranged using the simple relations

$$\begin{aligned}
\vec{M}_{stat} &= \frac{\overleftrightarrow{G}}{g_{eff}^2} \vec{z} \vec{M}^T \vec{z} \\
M_{i \text{ stat}} &= \frac{G_{iz}}{G_{zz}} M_z
\end{aligned} \quad (36)$$

to give

$$\begin{aligned}
& \overleftrightarrow{R} \left(\vec{M}(t) - \vec{M}_{eq} \right) \\
&= \vec{x} \left\{ \frac{1}{T_1} \frac{G_{xz}}{G_{zz}} (M_z - M_{z \text{ eq}}) + \frac{1}{T_2} \left(M_x - \frac{G_{xz}}{G_{zz}} M_z \right) \right\} \\
&+ \vec{y} \left\{ \frac{1}{T_1} \frac{G_{yz}}{G_{zz}} (M_z - M_{z \text{ eq}}) + \frac{1}{T_2} \left(M_y - \frac{G_{yz}}{G_{zz}} M_z \right) \right\} \\
&+ \vec{z} \left\{ \frac{1}{T_1} (M_z - M_{z \text{ eq}}) \right\}
\end{aligned} \quad (37)$$

This form allows a Bloch-like equation to be written in terms of observables from magnetic resonance measurements

$$\begin{aligned}
& \frac{\partial}{\partial t} \vec{M}(t) \\
&= \sigma \frac{\beta}{\hbar} \sqrt{\text{Det}(\overleftrightarrow{G})} \left\{ \overleftrightarrow{G}^{-1} \vec{M}(t) \times \vec{B} \right\} \\
&- \vec{x} \left\{ \frac{1}{T_1} \frac{G_{xz}}{G_{zz}} (M_z - M_{z \text{ eq}}) + \frac{1}{T_2} \left(M_x - \frac{G_{xz}}{G_{zz}} M_z \right) \right\} \\
&- \vec{y} \left\{ \frac{1}{T_1} \frac{G_{yz}}{G_{zz}} (M_z - M_{z \text{ eq}}) + \frac{1}{T_2} \left(M_y - \frac{G_{yz}}{G_{zz}} M_z \right) \right\} \\
&- \vec{z} \left\{ \frac{1}{T_1} (M_z - M_{z \text{ eq}}) \right\}
\end{aligned} \quad (38)$$

The energy of the interaction of the magnetic moment with the constant part of the magnetic field is $U = - \vec{B}_0^T \vec{M}$, and the spin-lattice relaxation process pushes the system toward its

equilibrium energy state, $U_{eq} = -\vec{B}_0^T \vec{M}_{eq}$. The energy of the PCs relaxes in the absence of the microwave $\vec{B}_1$ field as

$$\frac{\partial}{\partial t} U(t) = \frac{U_{eq} - U}{T_1} \quad (39)$$

Eq. (38) can be written using U as

$$\frac{\partial}{\partial t} \vec{M}(t) = \sigma \frac{\beta}{\hbar} \sqrt{\text{Det}(\vec{G})} \left\{ \vec{G}^{-1} \vec{M}(t) \times \vec{B} \right\} - \frac{U_{eq} - U}{T_1} \frac{\vec{G} \vec{B}_0}{\vec{B}_0^T \vec{G} \vec{B}_0} - \frac{1}{T_2} \left(\vec{M} + U \frac{\vec{G} \vec{B}_0}{\vec{B}_0^T \vec{G} \vec{B}_0} \right) \quad (40)$$

The U can be removed, allowing Eq. (38) to be written in two alternate forms emphasizing the similarity to the classic Bloch equations

$$\frac{\partial}{\partial t} \vec{M}(t) = \sigma \frac{\beta}{\hbar} \sqrt{\text{Det}(\vec{G})} \left\{ \vec{G}^{-1} \vec{M}(t) \times \vec{B} \right\} - \frac{1}{T_1} \frac{\vec{G} \vec{B}_0}{\vec{B}_0^T \vec{G} \vec{B}_0} \vec{B}_0^T (\vec{M} - \vec{M}_{eq}) - \frac{1}{T_2} \left(\vec{M} - \frac{\vec{G} \vec{B}_0}{\vec{B}_0^T \vec{G} \vec{B}_0} \vec{B}_0^T \vec{M} \right) \quad (41)$$

$$\frac{\partial}{\partial t} \vec{M}(t) = \sigma \frac{\beta}{\hbar} \sqrt{\text{Det}(\vec{G})} \left\{ \vec{G}^{-1} \vec{M}(t) \times \vec{B} \right\} - \frac{1}{T_1} \frac{\vec{G} \vec{z}}{\vec{z}^T \vec{G} \vec{z}} \vec{z}^T (\vec{M} - \vec{M}_{eq}) - \frac{1}{T_2} \left(\vec{M} - \frac{\vec{G} \vec{z}}{\vec{z}^T \vec{G} \vec{z}} \vec{z}^T \vec{M} \right) \quad (42)$$

which reduce cleanly to the isotropic Bloch equations, Eqs. (1-2), when the g tensor is isotropic. When the external magnetic field is directed along one of the principal axes of the tensor G , the relaxation term reduces to Eq. (2) but Eq. (30) is still needed to describe the elliptically-polarized precession of the magnetic moment.

The formulation of the Bloch equations in Eq. (42) is perhaps the most convenient form for understanding the evolution of the magnetic moment in a static magnetic field as illustrated in Fig. 3. The tip of the magnetic moment vector traces out an elliptical spiral path in a plane perpendicular to $\vec{B}_0$ at M_z so that the perpendicular components of $\vec{M}$ are elliptically

polarized but spiral in toward $\vec{M}_{eq}$ with a time constant T_2 , Fig. 3A. Meanwhile the plane containing the spiral relaxes toward a plane at $M_{z eq}$ with a time constant T_1 , Fig. 3B. This behaviour is qualitatively the same as for isotropic PCs. There is a precessing component of magnetization that relaxes with a time constant of T_2 and a component that does not precess that relaxes with a time constant T_1 . The additional complexity of Eqs. (38, 41-42) relative to the classical Bloch equations arises from the fact that the non-precessing component does not lie along $\vec{B}_0$. The additional elements in Eq. (38) describe the orientation of the non-precessing magnetization in space but do not increase the number of distinct relaxation times.

Relaxation times in one sense are independent of G anisotropy, and the time constants of T_1 and T_2 in Eqs. (38, 41-42) are independent of orientation or G anisotropy. However, T_1 and T_2 are set by the lattice variable $\vec{F}(t)$ in Eq. (14) which may introduce a dependence on G anisotropy depending on the details of how the PC interacts with the lattice [5].

Conclusions

A set of equations have been developed for spin $1/2$ systems with anisotropic g tensors. The equations describe the dynamics of the real physical observable, the magnetic moment

vector, in a combination of static and dynamic magnetic fields including relaxation caused by interactions with the lattice under the usual Redfield [8] and Wangsness and Bloch [9] conditions. The equations use only terms that are directly measurable in a magnetic resonance experiment: the magnetic moment vector, the $\vec{G}$ tensor and the signature σ of the g tensor.

In contrast, the Maxwell-Bloch and optical Bloch equations, usually used for this purpose, describe the dynamics of a fictitious spin, which is not a physical observable, using the g tensor, which is not directly measurable by magnetic resonance. Different conventions allow several different g tensors to be extracted from the same set of magnetic resonance measurements, leading to several potential descriptions of the anisotropic spin dynamics. In any event, the dynamics of the fictitious spin provides only limited insights into the dynamic magnetic properties of the real sample.

The free precession of the magnetic moment shows several differences from the behaviour of isotropic spins. In the absence of relaxation, the magnetic moment vector precesses around its equilibrium value, rather than around the external field. The precession does not cause any oscillating magnetic moment along the direction of the applied magnetic field; in fact, the length of the magnetic moment oscillates so that it traces out an ellipse in a plane perpendicular to the external magnetic field. This particular behaviour is a direct requirement for conservation of energy. The magnetic moment relaxes with two time constants, a T_1 and a T_2 . The T_2 relaxation can only affect some of the components of the magnetic moment vector perpendicular to the applied magnetic field. Only the T_1 relaxation can affect the component of the magnetic moment parallel to the field in addition to relaxing some of the perpendicular magnetization to its equilibrium value.

The signal measured by a typical pulse EPR spectrometer is induced in a resonator or coil by dM_x/dt during the free precession period. Anisotropic PCs can produce two signals, one from magnetization precessing near the PC Zeeman frequency with a decay constant of T_2^{-1} , and the other near zero frequency with a decay constant of T_1^{-1} . Because their intensities are proportional to dM_x/dt the signal near ω_0 is usually the one more easily detected.

One parameter in the equations is the signature, σ , of the g tensor. It is measurable by magnetic resonance using circularly-polarized microwave fields, but not in the reflection resonator standard in virtually all commercial EPR spectrometers. However, $\sigma=\pm 1$ affects only whether the magnetic moment precesses clockwise or counter-clockwise in response to a magnetic field. All other aspects of dynamics and relaxation are unaffected by σ so its value can continue to be routinely ignored.

Many applications of magnetic resonance to biological systems involve the interaction of metal-containing PCs with I 0 nuclei or other PCs. These include NMR of paramagnetic proteins [4], distance measurement by DEER [12, 13], and ENDOR spectroscopy, to name a few. They are based on the interaction of the PCs and nuclei through their magnetic moments [14] as isotropic and anisotropic hyperfine interactions or electron dipolar interactions. In the case of systems with large g anisotropy, the interaction may be called a pseudo-contact shift or other pseudo-type interaction [5]. The spectroscopy of such systems and the determination of spin Hamiltonian parameters from experimental spectroscopic measurements is well developed [15, 16]. The relaxation and dynamics of these systems considered here provides an opportunity to probe interactions not resolvable in CW EPR spectra.

Acknowledgments

This work was supported by the National Institutes of Health through R01GM069104 and R01HL095820 and by grant no. 5.6.1 of the Divisional project of the Russian Academy of Sciences 5.6. We appreciate helpful comments by Alexei A. Kipriyanov and valuable discussions on this subject with John Weil.

References

1. Bloch F. Nuclear Induction. *Physical Review*. 1946; 70:460–474.
2. Abragam, A. The principles of nuclear magnetism. Clarendon Press; Oxford: 1961.
3. Maryasov AG, Bowman MK. Spin dynamics of paramagnetic centers with anisotropic g tensor and spin of 1/2. *J Magn Reson*. 2012; 221:69–75. [PubMed: 22743542]
4. Bertini, I.; Turano, P. The Hyperfine Coupling. In: LaMar, GN., editor. *Nuclear Magnetic Resonance of Paramagnetic Macromolecules*. Kluwer Academic Publishers; Dordrecht: 1995. p. 29-54.
5. Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Ions*. Dover; New York: 1986.
6. Biedenharn, LC.; Louck, JD. *Advanced Book Program*. Addison-Wesley Pub. Co.; Reading, Mass: 1981. Angular momentum in quantum physics : theory and application.
7. Ernst, RR.; Bodenhausen, G.; Wokaun, A. *Principles of Nuclear Magnetic Resonance in One and Two Dimensions*. Clarendon Press; Oxford: 1987.
8. Redfield AG. Nuclear Magnetic Resonance Saturation and Rotary Saturation in Solids. *Physical Review*. 1955; 98:1787–1809.
9. Wangness RK, Bloch F. The Dynamical Theory of Nuclear Induction. *Physical Review*. 1953; 89:728–739.
10. Chibotaru LF, Ceulemans A, Bolvin H. Unique definition of the Zeeman-splitting g tensor of a Kramers doublet. *Phys Rev Lett*. 2008; 101:033003. [PubMed: 18764251]
11. Madelung, E. *Die mathematischen Hilfsmittel des Physikers*, 6., revidierte Aufl. ed. Springer; Berlin: 1957.
12. Jeschke G, Pannier M, Godt A, Spiess HW. Dipolar spectroscopy and spin alignment in electron paramagnetic resonance. *Chemical Physics Letters*. 2000; 331:243–252.
13. Milov AD, Maryasov AG, Tsvetkov YD. Pulsed Electron Double Resonance (PELDOR) and Its Applications in Free Radicals Research. *Applied Magnetic Resonance*. 1998; 15:107–143.
14. Weil, JA.; Bolton, JR.; Wertz, JE. *Electron paramagnetic resonance elementary theory and practical applications*. 2nd ed.. Wiley-Interscience; New York: 2007.
15. Weil, JA. On the Intensity of Magnetic Resonance Absorption by Anisotropic Spin Systems. In: Weil, JA.; Bowman, MK.; Morton, JR.; Preston, KF., editors. *Electronic Magnetic Resonance of the Solid State*. The Canadian Society for Chemistry; Ottawa: 1987. p. 1-19.
16. Schweiger A, Graf F, Rist G, Günthard Hs.H. Theory and applications of generalized operator transforms for diagonalization of spin Hamiltonians. *Chemical Physics*. 1976; 17:155–185.

- Spins are not directly observable, only the Magnetic Moment
- Magnetic Moment behaves differently than spin with g -anisotropy
- Bloch-like Equations for the Magnetic Moment with g anisotropy are derived
- The length of the Magnetic Moment oscillates to obey Conservation of Energy
- Relaxation of anisotropic Magnetic Moment has two relaxation times T_1 and T_2

Fig. 1.

In the absence of relaxation, the magnetic moment vector $\vec{M}$ shown as the thin black arrow precesses around its equilibrium direction M_{eq} in a static magnetic field as illustrated. The projection of $\vec{M}$ onto the external magnetic field $\vec{B}_0$ does not vary which conserves the total energy but the total length of $\vec{M}$ does vary as it precesses. The tip of $\vec{M}$ traces out an elliptical path in a plane perpendicular to $\vec{B}_0$, the components of $\vec{M}$ perpendicular to $\vec{B}_0$ are elliptically polarized as shown in their projection onto the x, y plane in the figure. Note that the path traced here does not include the origin in the x, y plane as it would in the case of isotropic PCs. The principal values of the g tensor are $\{1.0, 2.0, 4.0\}$ and

$$\vec{G} = \begin{pmatrix} 2.50 & 0.75 & -1.299 \\ 0.75 & 12.625 & 5.846 \\ -1.299 & 5.846 & 5.875 \end{pmatrix} \text{ in the laboratory frame. The initial } \vec{M}^T(0) = (0 \quad 0.323 \quad 0.353).$$

Fig. 2.

The trajectory of $\vec{M}$ during a microwave pulse is shown for an anisotropic PC as it follows a spiral path on the elliptic surface from Eq. (33). The system is assumed to be initially at equilibrium and relaxation is assumed to be negligible during the pulse. The trajectory is projected onto the x, y plane. At equilibrium, the M_{eq} lies at the spot on the ellipsoid having the maximum projection onto the applied field which is the lowest energy on the ellipsoid for the Hamiltonian in Eq. (7). The g and G tensors are the same as in Fig. 1.

Fig. 3.

(A) Trajectory of the magnetic moment vector $\vec{M}$ shown as the thin black arrow for negligible spin-lattice relaxation. $\vec{M}$ precesses around its equilibrium direction M^{eq} as illustrated but spirals inwards with a time constants of T_2 . The tip of $\vec{M}$ traces out an elliptical spiral in a plane perpendicular to $\vec{B}_0$ shown projected onto the x, y plane. (B) Trajectory of the magnetic moment vector $\vec{M}$ shown as the thin black arrow for $T_1/T_2 = 5$. $\vec{M}$ precesses around its equilibrium direction M^{eq} as illustrated but spirals inwards with a time constants of T_2 while the center of the spiral moves toward M_{eq} with a time constant of T_1 . The tip of $\vec{M}$ traces out a distorted elliptical spiral when projected onto the x, y plane. The g and G tensors and initial $\vec{M}$ are the same as in Fig. 1.