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Anisotropic $S = 1/2$ Kramers Doublets: g-Matrix, the Tensor G, and Dynamics of the Spin and Magnetic Moment

Alexander G. Maryasov[1] · **Michael K. Bowman**[1,2]

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Abstract
The properties and dynamics of isotropic electron spins are drastically simpler than for anisotropic spin systems with $S = 1/2$. The classical rotating coordinate frame with axes moving at the microwave frequency provides convenient descriptions of isotropic electron spins, their magnetic moments and their magnetic resonance behavior but does not provide a suitable description for paramagnetic centers having significant anisotropy in their $\overleftrightarrow{g}$ matrix. The relative merits of several different frames are discussed including the laboratory frame, a tilted rotating frame and effective field frames. It is seen that simulations of the anisotropic spins are more easily performed with a different frame for each orientation of the spin, but results can be readily visualized in the laboratory frame.

1 Introduction

Magnetic resonance is increasingly used to investigate, characterize and design materials with novel magnetic, optical, spin and quantum properties for a variety of new technologies ranging from novel catalysts, MRI contrast agents and spin labels; through quantum communications and computation; to functional nanomolecular devices. The coupling of the electron spin angular momentum with additional spin, orbital or rotational angular momentum in such systems can present magnetic resonance spectroscopists with very large anisotropies requiring broad spectral windows and has helped drive the development of high-frequency EPR [1, 2] and a more general description of magnetic resonance. The relatively isotropic electron spins in the

✉ Alexander G. Maryasov
maryasov@nioch.nsc.ru

Michael K. Bowman
mkbowman@ua.edu

[1] N.N.Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russia

[2] Department of Chemistry & Biochemistry, The University of Alabama, Tuscaloosa, AL 35487, USA

s- and p-orbitals of light elements allow the electron spin and its magnetic moment to be used almost interchangeably and makes the rotating frame a convenient framework for discussing a wide range of magnetic resonance experiments. However, in highly anisotropic spin systems, the electron's spin and angular momentum have significantly different behaviors and it is necessary to consider several sets of axes or frames to describe and interpret magnetic resonance experiments.

In this paper, we examine some of the fundamental differences in the behavior of very anisotropic doublet spins systems and some convenient frames for describing resonance experiments. Most EPR spectra have their origin in the spins of electrons and it seems natural to think of EPR in terms of the electron spin. Such an approach works well for isotropic systems, but as we shall see, it quickly becomes very complicated and inconvenient for highly anisotropic systems. The fundamental difficulty lies in the fact that the measured EPR signal is nearly always derived from a classical magnetic dipole: a macroscopic observable of the quantum system. A classical magnetic dipole interacts with a magnetic field; there is a contribution to the potential energy of the system and a dynamic exchange of energy or force acting on the dipole. This makes it natural to consider magnetic resonance in terms of the classical macroscopic magnetic moment resulting from a large number of moments from the individual paramagnetic centers (PCs) in a sample. The microwave (mw) radiation can be considered as a classical oscillating magnetic field composed of a large number of coherent photons, each much smaller than the thermal energy, kT. This approach allows most magnetic resonance experiments to be described by the classic interaction of a magnetic dipole in a magnetic field, although completely quantum mechanical descriptions in terms of dressed quantum states of spins and photons are possible.

But utilizing such a classical description means we should speak in terms of magnetic moments instead of electron spins because there is no classical 'spin' and consequently an electron's spin has no classical interaction with a magnetic field. However, one property of a spin is its magnetic moment $\hat{\vec{\mu}}$, given in dimensionless form as

$$\hat{\vec{m}} = -\hat{\vec{\mu}}/\beta = \vec{\vec{g}}\hat{\vec{S}} \tag{1}$$

with the minus sign explicitly taking account of the negative charge of the electron. So whatever is done to the magnetic moment immediately affects the spin. For the isotropic PC, $\vec{\vec{g}}$ is readily replaced by the scalar g-factor: the spin and its magnetic moment always point in the same direction, they evolve identically in time, and their projections in any direction are always proportional. It seems natural to use $\hat{\vec{m}}$ or $g\hat{\vec{S}}$ interchangeably, which contributes to the utility of the rotating frame for isotropic PCs, as described below.

On the other hand, for the anisotropic PC, $\vec{\vec{g}}$ is a matrix [3], so that generally its $\hat{\vec{m}}$ and $\hat{\vec{S}}$ point in different directions; the length of $\hat{\vec{m}}$ varies whereas $\hat{\vec{S}}$ has a constant length of $\sqrt{S(S+1)}$; and they evolve differently during magnetic resonance experiments. Since they are no longer interchangeable, the magnetic moment and the spin demand a more consistent treatment which can be done with the use of several frames. We will examine several of the more useful frames and contrast

the properties of the spin and magnetic moment in the context of magnetic resonance of a PC with $S = 1/2$.

2 The Frames

We first introduce the traditional lab frame with axes $\vec{b}_1, \vec{b}_2, \vec{b}$ that are related to the spectrometer. For convenience, we will often use the verbal shorthand of referring to the first, second, and third axes of a frame by some variants of the letters x, y, and z, respectively. The vector $\vec{b}$ is directed along the direction of the static magnetic field so that $\vec{B}_0 = B_0\vec{b}$ and is used as the z-axis direction for the lab frame. The vector $\vec{b}_1$ is directed along the x-axis of the lab frame. Nearly all commercial spectrometers have a linearly polarized mw magnetic field that excites the sample and detects the EPR signal so the direction of the mw magnetic field at the sample is taken as the direction of $\vec{b}_1$. The vector $\vec{b}_2$ is the y-axis of the lab frame, perpendicular to the two first vectors so that the frame is right-handed.

The next frame we introduce is the "effective field" frame (EFF) with axes $\vec{k}_1, \vec{k}_2, \vec{k}$, where the Zeeman interaction of the PC is diagonal. If the PC is isotropic, then the EFF and the lab frame coincide; the spin is said to be quantized along the direction of the magnetic field $\vec{B}_0$. That is, the projection of the spin onto the z'-axis of the EFF (which is parallel to $\vec{b}$ or to $\vec{k}$ in the isotropic and anisotropic cases, respectively) does not evolve in time in the absence of a perturbation, e.g., a mw magnetic field; but the projections of the spin onto the x'- and y'-axes (i.e., $\vec{k}_1, \vec{k}_2$) do evolve and interchange as described by the Bloch equations. The Zeeman interaction portion of the Hamiltonian of a PC, $\hat{H}_Z$, in an external magnetic field, $\vec{B}$, is

$$\hat{H}_Z = \beta\vec{B}^{\mathrm{T}}\hat{\vec{m}}. \tag{2}$$

Making use of Eq. (1), the Hamiltonian may be rewritten as if the Zeeman interaction were the interaction of the PC spin with an effective magnetic field, $\vec{B}_{\mathrm{eff}}$,

$$\hat{H}_Z = -\beta\vec{B}_{\mathrm{eff}}^{\mathrm{T}}\hat{\vec{S}}. \tag{3}$$

The effective field can be written as

$$\vec{B}_{\mathrm{eff}}^{\mathrm{T}} = \vec{\vec{g}}^{\mathrm{T}}\vec{B}. \tag{4}$$

In magnetic resonance, the magnetic field is usually the sum of a constant $\vec{B}_0$ which defines the energy levels of a PC and a rapidly oscillating mw part, $\vec{B}_1 = B_1(t)\vec{b}_1$, which causes resonance transitions between those energy levels,

$$\vec{B} = B_0\vec{b} + B_1(t)\vec{b}_1. \tag{5}$$

For an anisotropic PC, the EFF is the quantization direction of the spin, i.e., the z'-axis, generally not parallel to $\vec{b}$, but rather to

$$\vec{k} = \frac{\overleftrightarrow{g}^{\mathrm{T}}\vec{b}}{g_{\mathrm{eff}}}, \tag{6}$$

where g_{eff} is the effective value of the g-tensor [3], $g_{\mathrm{eff}} = \sqrt{\vec{b}^{\mathrm{T}}\overleftrightarrow{G}\vec{b}} = \sqrt{G_{zz}}$ and $\overleftrightarrow{G} = \overleftrightarrow{g}\overleftrightarrow{g}$. The $\vec{k}$ vector gives the direction of the "effective field" along which the spin is quantized. The $\vec{k}_1$ vector is the x'-axis of the EFF and lies along the direction of the effective mw field ($B_1\vec{K}_1 = B_1\overleftrightarrow{g}\,\vec{b}_1$), perpendicular to $\vec{k}$ with

$$\vec{k}_1 = \frac{\left\{\vec{K}_1 - \vec{k}\left(\vec{k}\cdot\vec{K}_1\right)\right\}}{g_1}, \tag{7}$$

and

$$g_1 = \sqrt{G_{xx} - G_{xz}^2/G_{zz}}. \tag{8}$$

The vector $\vec{k}_2$ defines the y' axis of the EFF and may be calculated as

$$\vec{k}_2 = \vec{k}\times\vec{k}_1 \tag{9}$$

to provide the right-handed frame of $\vec{k}_1, \vec{k}_2, \vec{k}$. Detailed derivations of these axes are described in [4–6]. This EFF smoothly converges to the lab frame as the $\overleftrightarrow{g}$ matrix becomes isotropic and then $\overleftrightarrow{g}$ can be replaced by a scalar g-factor. We note, that the transformation from the lab frame to the EFF may be written symbolically as $\left\{\vec{k}_1, \vec{k}_2, \vec{k}\right\} \propto \overleftrightarrow{g}^{T}\left\{\vec{b}_1, \vec{b}_2, \vec{b}\right\}$. It is important to realize here that Eq. (9) is used to calculate the direction of y'-axis instead of a procedure similar to that for the x'-axis given in Eqs. (7, 8). The issue is that the $\overleftrightarrow{g}$ matrix in the general case may convert the right-handed frame to a left-handed one, if the matrix signature, σ, is negative. The matrix signature is the sign of its determinant,

$$\sigma = \mathrm{sign}\left(\det\left(\overleftrightarrow{g}\right)\right), \tag{10}$$

determines the precession direction of the magnetic moment [3, 5, 6], and so Eq. (9) preserves the handedness of the frames.

It is useful at this point to consider the spin, the magnetic moment and how they evolve in the absence of a mw field. This is relatively easy in the EFF where we can easily write the projections or x', y', z' components of the spin on the axes of the EFF as

$$\hat{\vec{S}} = \hat{S}_{x'}\vec{k}_1 + \hat{S}_{y'}\vec{k}_2 + \hat{S}_{z'}\vec{k}. \tag{11}$$

The mw field is readily included but provides no additional insights while making the equations even more complicated. We can use Eq. (1) to obtain the dimensionless magnetic moment as

$$\hat{\vec{m}} = \vec{\vec{g}}\left(\hat{S}_{x'}\vec{k}_1 + \hat{S}_{y'}\vec{k}_2 + \hat{S}_{z'}\vec{k}\right) = \hat{S}_{x'}\left\{\vec{\vec{g}}\vec{k}_1\right\} + \hat{S}_{y'}\left\{\vec{\vec{g}}\vec{k}_2\right\} + \hat{S}_{z'}\left\{\vec{\vec{g}}\vec{k}\right\}. \quad (12)$$

For isotropic PCs, $\vec{\vec{g}}$ in Eq. (12) can be replaced by the isotropic g-value, revealing that the projections of $\hat{\vec{m}}$ along the $\vec{k}_1, \vec{k}_2, \vec{k}$ directions are clearly proportional to the spin. In fact, one can say, e.g., that the x' component of the magnetic moment comes from (or is equivalent to) the x' component of the spin, making it easy to ignore the distinction between magnetic moment and spin for isotropic PCs.

However, when the PC is anisotropic, a vector on the right-hand side of Eq. (12), e.g., $\left\{\vec{\vec{g}}\vec{k}_1\right\}$, generally no longer is parallel to $\vec{k}_1$, but includes components along $\vec{k}_2$ and $\vec{k}$. Thus, e.g., $\hat{S}_{x'}$ contributes not only to $\hat{m}_{x'}$, but also to $\hat{m}_{y'}$ and $\hat{m}_{z'}$ along the $\vec{k}_2$- and $\vec{k}$-directions, respectively. Exactly where the axes of the EFF point depends on the $\vec{\vec{g}}$ matrix which is tied to the orientation of the PC in the lab frame. Thus, in a sample with randomly oriented PCs, we must deal with not one EFF, but with an ensemble of frames, each having its own particular properties and orientation in the lab frame. In a single crystal, the number of distinct EFFs may be reduced to a manageable number, depending on the sites a PC may occupy in the elementary crystal cell.

The difference between the lab frame and the EFFs can produce unexpected effects with very anisotropic spins because of the difference between the directions of the 'z'-axes of these two frames: $\vec{k}$ versus $\vec{b}$. For PCs at equilibrium, the $\hat{S}_{z'}$ parallel to the direction of quantization is the only non-zero component of the spin and is time independent in the absence of a mw magnetic field or other perturbation. However, this spin component is generally not along the direction of the magnetic field $\vec{B}_0$, it lies at some angle to $\vec{B}_0$, yet does not precess around $\vec{B}_0$; surprises for those accustomed to isotropic PCs. In addition, an $\hat{S}_{x'}$ or $\hat{S}_{y'}$ component in Eq. (11) will precess around $\vec{k}$, but usually with a spin component oscillating along the $\vec{B}_0$-direction even in the absence of a mw field. But energy must be conserved, so that the energy of the system must not change as spins periodically align along or opposite to $\vec{B}_0$. This apparent paradox occurs because there is no direct interaction between the spin and the magnetic field. It is the magnetic moment that interacts with the field. Even though a component of the spins oscillates along the $\vec{B}_0$ direction, the magnetic moment precesses in a plane perpendicular to $\vec{B}_0$ in this situation, so that the total energy is conserved and constant [6]. Only the $\hat{m}_x$ component of the magnetic moment, parallel to the lab frame $\vec{b}_1$, induces the EPR signal into the linearly polarized mw mode of conventional resonators [7] because the resonator mode resides in the laboratory frame and not in the EFF.

3 Discussion

The well-known rotating frame is an extension of the lab frame for isotropic PCs in which the rapid oscillations of the mw field and the x and y projections of the spins or magnetic moments are removed by having the x- and y-axes rotate synchronously with the mw field. The rotating frame in magnetic resonance is one specific version of the interaction representation or Dirac picture of quantum mechanics. The

rotating frame is very useful because it takes advantage of two fundamental characteristics of isotropic spins: a) the spin or magnetic moment retains its magnitude as it precesses around $\vec{B}_0$ (or the effective field); and b) the motion is perpendicular to $\vec{B}_0$ (or the effective field). These features convert the spin or magnetic moment to a circularly polarized vector. The linearly polarized mw field in the lab frame can be written as a sum of two circularly polarized fields. Resonant spins and their magnetic moments move together with one of the circularly polarized mw fields and respond strongly to that field. The other circularly polarized field reverses every quarter cycle of the mw frequency, immediately undoing whatever effect it had on the spins or moments and consequently can be ignored. This rotating frame is easily applied to isotropic PCs because the spins and their magnetization have axial symmetry in the plane perpendicular to $\vec{B}_0$, so that only a single circularly polarized component needs to be considered for each set of spins having the same EPR frequency. The result is that rapid oscillations of the mw field are removed in the rotating frame so that the much slower nutations and relaxations of the spins and their magnetic moments can be readily visualized and intuitively predicted.

However, in most orientations, the very anisotropic PCs lack such symmetry, at least in their magnetic moments. An elliptically polarized magnetic moment is present (usually tilted with respect to $\vec{B}_0$) which must be represented by two circularly polarized components with different amplitudes. Magnetic resonance of such PCs then needs to consider the responses of both circularly polarized magnetic moment components with the similarly polarized mw fields. In addition, the mw fields and relaxation interconvert and partially mix the magnetic moment components. Both components vectorially combine to produce the magnetic resonance signal in the mode of the mw resonator residing back in the lab frame. These and other complications negate the major advantages that the rotating frame provides for isotropic PCs [7]. When applied correctly with very anisotropic PCs, the rotating frame becomes even more complicated than the lab frame, and when used incorrectly, it produces incorrect results.

Nevertheless, some simplification of the spin motion is still possible in a type of tilted rotating frame (TRF) [5] derived from the EFF $\vec{k}_1, \vec{k}_2, \vec{k}$. A linearly polarized mw field in the lab frame is also linearly polarized in the EFF, directed along the vector $\vec{K}_1$. Its projection onto the $\vec{k}_1$-direction will induce transitions in the spin system whereas its projection onto the effective field $\vec{k}$ rapidly but adiabatically modulates the energy levels, with negligible effect on spin dynamics. The spin vector does not change amplitude as it precesses around the effective field, so it can be represented by a single circularly polarized component. As in the standard rotating frame we only need to consider the component of the effective mw field rotating around the electron spin quantization axis $\vec{k}$ at the mw frequency and can represent the linearly polarized effective mw field component along $\vec{k}_1$ as a sum of two oppositely rotating fields, one of which is in resonance with spin precession and the other off-resonance and rotating rapidly in the opposite direction. This means that in the TRF, spin dynamics may be described in a manner similar to spin dynamics of isotropic PCs in the standard rotating frame. The important difference is that all measurable quantities require additional use of Eq. (1) and conversion back to the lab frame because the signals in magnetic

resonance experiments are induced in the resonator, back in the lab frame, by the magnetic moments of the PCs, see discussion in [8]. Another issue is that in a disordered system we must consider the ensemble of TRFs related to different orientations of the anisotropic PCs with respect to the lab frame because each EFF has its own specific TRF. As with the conventional rotating frame, incorrect application of the TRF will produce incorrect results.

The rotating frame enables a straightforward derivation of the Bloch equations, but the Bloch equations have been extended to spectroscopies quite different from magnetic resonance of isotropic PCs. Thus, one could expect that in the proper frame, it would be possible to develop Bloch-like equations even for very anisotropic PCs. Unfortunately, neither the lab frame, nor the EFF, nor the TRF give a simple, consistent or reasonable description of spins or magnetic moments for anisotropic PCs.

The lab frame functions well for isotropic spins because it was built around the applied magnetic field that is the quantization axis for isotropic spins. At equilibrium with no applied mw fields, the spin projection onto $\vec{B}_0$ is time independent and the spin projection on directions perpendicular to $\vec{B}_0$ is zero. The EFF and the TRF have similar characteristics for the spin of isotropic and anisotropic PCs: at equilibrium with no applied mw fields, the spin projection onto $\vec{k}$ is time independent and the spin projections perpendicular to $\vec{k}$ are zero. Yet these frames with their focus on spin do not yield a simple, consistent picture of the spin or magnetic properties of anisotropic PCs. We, therefore, turn to a more complicated frame that overcomes some of the problems of the EFF.

Rather than focusing on the quantization direction of spins, this frame will focus on the magnetic moments. The quantization or 'z'-axis direction for the previous frames is the direction, Eq. (6), of the equilibrium spin $\vec{S}_{\text{eq}}$ in the absence of a microwave field. An analogous treatment for the magnetic moment uses the equilibrium magnetization $\vec{M}_{\text{eq}}$ as the 'z'-direction. We will call it the $\vec{M}_{\text{eq}}$ frame with

$$\vec{M}_{\text{eq}} = \frac{\beta^2}{4kT}\overleftrightarrow{G}\vec{B}_0. \tag{13}$$

This $\vec{M}_{\text{eq}}$ frame has been used to build Bloch-like equations for the motion of the magnetic moment $\vec{\hat{m}}$ [6]. It is able to model a range of magnetic resonance phenomena including transient nutations, free induction decays and T_1 and T_2 relaxation. It also is based on classical interactions between magnetic dipole moments and magnetic fields. However, this frame does have some peculiarities. In simplest form, the axes are not orthogonal to each other. The magnetization precesses around the direction of the equilibrium magnetization $\vec{M}_{\text{eq}}$ in the absence of a mw field or relaxation, but in a plane perpendicular to $\vec{B}_0$ and generally tilted relative to $\vec{M}_{\text{eq}}$. This means that the magnitude of the magnetization $|\vec{m}|$ oscillates at harmonics of the EPR frequency. Just as with the EFF for anisotropic PCs, a different $\vec{M}_{eq}$ frame is required for each distinct orientation of a PC and its $\overleftrightarrow{g}$ matrix. But for an ensemble of identical, oriented PCs, the Bloch-like equations can be written as

$$\frac{\partial \vec{m}(t)}{\partial t} = \sigma \frac{\beta}{\hbar} \sqrt{\mathrm{Det}\left(\overleftrightarrow{G}\right)} \left(\overleftrightarrow{G}^{-1} \vec{m}(t) \times \vec{B} \right) - \frac{1}{T_1} \frac{\overleftrightarrow{G}\vec{B}_0}{\vec{B}_0^{\mathrm{T}} \overleftrightarrow{G} \vec{B}_0} \vec{B}_0^{\mathrm{T}} \left(\vec{m}(t) - \vec{M}_{\mathrm{eq}} \Big/ \beta \right) - \frac{1}{T_2} \left(\vec{m}(t) - \frac{\overleftrightarrow{G}\vec{B}_0}{\vec{B}_0^{\mathrm{T}} \overleftrightarrow{G} \vec{B}_0} \vec{B}_0^{\mathrm{T}} \vec{m}(t) \right) \tag{14}$$

with σ being the signature of the $\overleftrightarrow{g}$ matrix, Eq. (10), which defines the direction of magnetic moment precession [3]. Equation (14) for the magnetic moment has the form of the Bloch equations but the coefficients are complicated and difficult to visualize. This is not surprising considering the non-orthogonal $\vec{M}_{\mathrm{eq}}$ frame from which it was developed. However, Eq. (14) is quite useful for calculating the dynamics and behavior of $\vec{m}$, but the results are more easily visualized in the $\vec{M}_{\mathrm{eq}}$ frame when considering a single orientation of the PC or in the lab frame when more than one orientation is considered. This is demonstrated for the rather anisotropic PC discussed in [6].

The PC begins with $\left(g_x, g_y, g_z\right) = (1.0,\ 2.0,\ 4.0)$ in the lab frame, but the PC is rotated by $\pi/4$ around $\vec{B}_0$ and then by $\pi/3$ around $\vec{b}_1$, giving $\vec{M}_{eq}$ that points, Fig. 1a, in a very different direction from $\vec{B}_0$ (and the spin $\vec{k}$). For comparison, a second orientation is generated by a further rotation of the PC by an additional $\pi/4$ around $\vec{B}_0$, Fig. 1b. This additional rotation leaves the EPR frequency

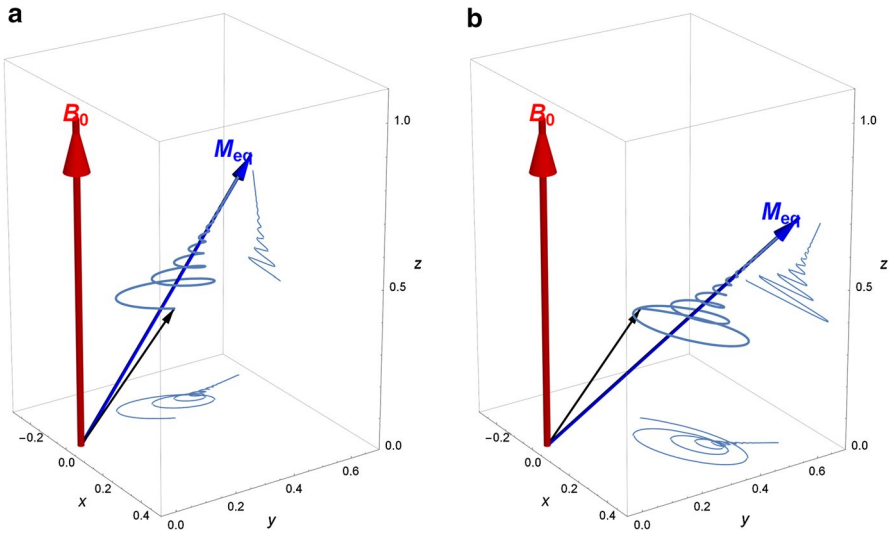

Fig. 1 Evolution magnetic moments of two orientations of PCs in the lab frame. **a**, **b** Orientations differ by a $\pi/4$ rotation around $\vec{B}_0$ so that EPR frequencies are identical for the two sets of PCs but they have different $\vec{M}_{\mathrm{eq}}$ frames. The red vector is the direction of the external magnetic field $\vec{B}_0$, the blue vector shows $\vec{M}_{\mathrm{eq}}$ for each PC orientation and the black vector the magnetic moments $\vec{m}(0)$ at the start of their evolution. See the text for further details (color figure online)

identical for these two PC orientations but causes profound differences in many other properties. For example, the $\vec{M}_{eq}$ for these two sets of PCs are quite different from each other and consequently they have quite different $\vec{M}_{eq}$ frames, Fig. 1. Let us consider the evolution of the two sets of PCs after preparing them in the 'same' $\vec{m}(0) = (0., 0.323, 0.353)$ initial state indicated by the black vector, Fig. 1a, b. The blue curve traces the motion of the tip of $\vec{m}(t)$ as it evolves and relaxes with $T_1 = 5T_2$ in the absence of a mw field.

The $\vec{m}(t)$ from the PCs with different orientations start from the same location in the lab frame at $t = 0$ but immediately diverge and spiral/relax toward their own $\vec{M}_{eq}$. If there were no relaxation, the $\vec{m}(t)$ would trace out ellipses around their $\vec{M}_{eq}$ vector, in a plane tilted relative to $\vec{M}_{eq}$ but perpendicular to $\vec{B}_0$. Projections of $\vec{m}(t)$ onto the x,y plane are shown at the bottom and onto the x, z plane on the right-hand side of the lab frames, Fig. 1a, b. The projections in the x-direction induce the EPR signal in the usual linearly polarized EPR resonator. The projections on the x, z plane show rapid oscillations along x at the EPR frequency that decay with a time constant T_2 and a slower T_1 relaxation approaching the projections of $\vec{M}_{eq}$. Although the initial $\vec{m}(0)$ are identical for the two sets of PCs, Fig. 1a, b, their projections on the x-direction show they would produce free induction decays in the resonator with opposite phase and different amplitudes but the same frequency.

One important feature of isotropic PC dynamics in the absence of relaxation is that the lengths of both spin and magnetic moment are conserved for arbitrary values of external magnetic field strength and direction. These vectors rotate around the instantaneous direction of the magnetic field at their respective instantaneous angular frequency. In the case of the anisotropic PCs, the behavior of these vectors differs. Their spin rotates in a similar way but around their own individual effective field direction, whereas their magnetic moment length varies, always touching the surface of a 3D ellipsoid in each $\vec{M}_{eq}$ frame given by the equation

$$\vec{m}^{\mathrm{T}}(t)\overleftrightarrow{G}^{-1}\vec{m}(t) = \text{const} \tag{15}$$

with the constant depending on the initial conditions [6].

This brief example illustrates some of the problems encountered with very anisotropic PCs and tries to highlight aspects that prevent the direct application of the rotating frame to very anisotropic systems. Even if the PCs have identical EPR frequencies and are prepared in the same initial state, the subsequent evolution, dynamics and properties at equilibrium can be very different, so that each orientation of a PC with significant $\overleftrightarrow{g}$ anisotropy must be treated individually in its own $\vec{M}_{eq}$ frame. Then each EFF or $\vec{M}_{eq}$ frame must be projected back into the lab frame where the EPR spectrometer or detection apparatus resides. Yet Eq. (14) and the $\vec{M}_{eq}$ frame provide a foundation for the description and calculation of the dynamics of the magnetization in resonance experiments.

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