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Theory of EPR on a rotating sample: An illustration of Berry's phase

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Abstract. We describe the theory of EPR in a crystal field multiplet under sample spinning. Berry phases arise because the crystal field is of lower symmetry than the full rotation group. The formal development is limited to pure J multiplets, crystal field doublets, and field and rotation axes parallel to a principal axis.

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1 Introduction

The object of this article is the analysis of the influence of sample rotation on the electronic resonance of paramagnetic ions in a monocrystalline solid. It will eventually lead to well-defined predictions for the outcome of well-defined experiments, in the perspective of forthcoming implementation of these experiments. The starting principle of this work is schematically as follows. In a crystalline solid, a paramagnetic ion experiences a crystal field in which its spectrum consists of manifolds corresponding to irreducible representations of the crystal field symmetry group. If the crystal is subjected to a rotation which does not belong to this group, the new eigenkets of each manifold will be linear combinations of initial eigenkets from different manifolds. Experimental evidence for such a mixing has been obtained from the study of the contribution of phonon rotational modes to electronic relaxation [1]. In the course of a continuous rotation, each eigenket of the Hamiltonian will follow a circuit in a Hilbert space, which can be transcribed into a circuit in the space of the parameters characterizing the rotation. If the latter is adiabatic, the physical situation is directly connected to the concept of geometric phases, whose modern emergence arose from the work of Berry [2], and which are now generally known as Berry's phases. Under its most general form, the concept of Berry phases appears for any arbitrary oscillating system subjected to a perturbation of low frequency. During its slow adiabatic evolution, the system acquires, in addition to a dynamic phase, an extra phase of purely topological character. In the problem we will study: EPR on a rotating sample, Berry's phase will show up by a modification of the resonance spectrum.

We recall briefly the steps which brought Berry's phase concept to general attention. Berry's article of 1984 [2] dealt with an improved description of the long-known Adiabatic Theorem [3], for a non-degenerate eigenstate of a periodic Hamiltonian, and considered the topologic phase accumulated after one evolution period. The theory was soon extended to the adiabatic evolution of degenerate states [4,5] as well as to the non-adiabatic but cyclic evolution of quantum states [6]. It was realized from the start that geometric phases could be described in the language of parallel transport in fiber bundles [7]. A remarkably clear introduction to this connection can be found in [8, 9]. Most of these developments are described in a review article [10] and in a book originating from a workshop [11]. References to experimental illustrations can be found in these publications. Many more have been performed since. We restrict ourselves to some of those performed in NMR [12–16], which is particularly suited to such illustrations, because of the versatility of manipulation of nuclear spins it affords. Detailed studies have been performed on both adiabatic and non adiabatic geometric phases on nuclei subjected to a rotating magnetic field or to rf pulses, or nuclei subjected to an axial quadrupole interaction under simple or double sample spinning.

The phenomenon of geometric phases is very general. It is associated with a mathematic structure met in a wide class of physical problems, both in classical and in quantum systems. It has the quality of being a unifying formal link between theoretical developments made independently in many fields of physics. This does not deprive these former tools from their practical usefulness. In the following, the theory of EPR under sample spinning is made within the quantum formalism of changes of representation [17], a standard procedure for magnetic resonance. The first instance was that of the rotating frame picture for pure Zeeman resonance [18], which has a simple geometric interpretation. It was later extended to more complex cases: pure quadrupole interaction [19], for which

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there is no simple geometric picture, and multiple pulse methods [20] with a series of rotations around different axes in the rotating frame, leading to the so-called "toggling frame" picture [21]. The same method was used in connection with geometric phases in [13,16,22], and also partly in [12].

The article is organized as follows. Section 2 is a brief summary of the change of representation method, in a general but simplified form adapted to describing resonance. Section 3 is devoted to the theory of EPR, derived in turn for pulsed and CW observation. We analyze only the case of crystal field doublets in J multiplets. Finally, the Appendix discusses briefly the connection of the present theory with the mathematical approach of parallel transport.

2 The change-of-representation method

The present description duplicates somewhat that of reference [22], Section V, but is given in a more explicit fashion.

Let a quantum system evolve under a continuous time-dependent Hamiltonian, whose forms at different times do not always commute, and such that:

- its eigenspectrum consists of states well-separated in energy, degenerate or not,
- in the course of time, they remain well-separated,
- the time evolution is slow with respect of the large energy splittings.

The evolution operator $U(t)$ evolves according to:

$$\frac{\mathrm{d}}{\mathrm{d}t}U(t) = -i\mathcal{H}(t)U(t). \tag{1}$$

Let us write:

$$\mathcal{H}(t) = U_0(t)\mathcal{H}_0(t)U_0^\dagger(t) \tag{2}$$

where:

- the eigenvalues of $\mathcal{H}_0(t)$ are the same as those of $\mathcal{H}(t)$, a mere consequence of equation (2),
- the eigenstates of $\mathcal{H}_0(t)$ are the same as those of $\mathcal{H}\,(0)$. Then, at all times:

$$[\mathcal{H}_0(t), \mathcal{H}(0)] = 0 \tag{3}$$

and the geometric "travel" of the eigenstates of $\mathcal{H}\,(t)$ in the Hilbert space is completely determined by the unitary operator $U_0(t)$. We write its derivative as:

$$\frac{\mathrm{d}}{\mathrm{d}t}U_0(t) = \dot{U}_0(t) = -iA(t)U_0(t). \tag{4}$$

We perform a change of representation by writing:

$$U(t) = U_0(t)\tilde{U}(t) \tag{5}$$

whence:

$$\dot{U}(t) = \dot{U}_0(t)\tilde{U}(t) + U_0(t)\,\dot{\tilde{U}}\,(t) \tag{6}$$

that is, according to equations (1, 4):

$$-i\mathcal{H}(t)U(t) = -iA(t)U_0(t)\tilde{U}(t) + U_0(t)\,\dot{\tilde{U}}\,(t) \tag{7}$$

and, according to equations (2, 5):

$$\begin{aligned} -iU_0(t)\mathcal{H}_0(t)U_0^\dagger\,(t)\,U_0(t)\tilde{U}(t) &= -iU_0\mathcal{H}_0\tilde{U} \\ &= -iAU_0\tilde{U} + U_0\,\dot{\tilde{U}}\,. \end{aligned} \tag{8}$$

We multiply all terms on the left by $U_0^\dagger(t)$ and we obtain:

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{U} = -i\left(\mathcal{H}_0 - U_0^\dagger AU_0\right)\tilde{U} \tag{9}$$

a standard result for a change of representation. The evolution is adiabatic if the matrix elements of $U_0^\dagger AU_0 = \tilde{A}\,(t)$ between different states of $\mathcal{H}_0$ are small compared with their splitting. To the lowest order of perturbation, we may then forget about these matrix elements and truncate $\tilde{A}(t)$ so as to retain only that part which commutes with $\mathcal{H}_0(t)$, say $\tilde{A}'(t)$. Higher orders in perturbation theory yield corrections to the adiabatic approximation. We neglect them here. The evolution of $\tilde{U}(t)$ is then described by the equation:

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{U}(t) = -i\mathcal{H}_{\mathrm{eff}}(t)\tilde{U}(t) \tag{10}$$

with:

$$\mathcal{H}_{\mathrm{eff}}(t) = \mathcal{H}_0(t) - \tilde{A}'(t) \tag{11}$$

whose eigenstates are the same as those of $\mathcal{H}(0)$. As a consequence:

- $\tilde{U}(t)$ does not change the eigenstates of $\mathcal{H}_0(t)$, but only their phases,
- the term $\mathcal{H}_0(t)$ gives rise to the dynamic phase, whereas $\tilde{A}'(t)$ contributes to the topological phase,
- $U_0(t)$, which changes the eigenstates of $\mathcal{H}_0(t)$ into those of $\mathcal{H}(t)$, may also contribute to the topological phase.

For a cyclic evolution of $\mathcal{H}(t)$ with period T, we may choose U_0 so that $U_0\,(T) = 1$, in which case the topological phase after each cycle arises entirely from $\tilde{A}'(t)$. Let $\tilde{A}'_\eta(t)$ be the projection of $\tilde{A}'$ onto an eigenmanifold $\{\eta\}$ of $\mathcal{H}_0$. The Berry phase in that subspace is obtained from:

$$K(T) = \mathrm{T}\exp\left\{i\int_0^T \tilde{A}'_\eta(t')\mathrm{d}t'\right\} \tag{12}$$

where T is the chronological operator.

If $\{\eta\}$ is non-degenerate, $\tilde{A}'_\eta(t)$ is a real c-number. If $\{\eta\}$ is p-fold degenerate, $\tilde{A}'_\eta(t)$ is a $p\times p$ matrix, and we may have

$$\left[\tilde{A}'_\eta\,(t_1)\,, \tilde{A}'_\eta\,(t_2)\right] \neq 0.$$

If the eigenkets of $\mathcal{H}(t)$ depend on several parameters λ_i (for instance polar angles θ and φ, or Euler angles α, β, γ in ordinary space), then $U_0\,(t)\,, \tilde{A}'(t)$ and $\tilde{A}'_\eta(t)$ depend on the same parameters, *i.e.:*

$$\tilde{A}'_\eta(t) = \tilde{A}'_\eta\left[\lambda_i(t)\right]. \tag{13}$$

In the integrand of equation (12), we may then replace $\tilde{A}'_\eta(t')\,\mathrm{d}t'$ by

$$\tilde{A}'_\eta(t')\,\mathrm{d}t' \;\longrightarrow\; \sum_i \tilde{A}'_{\eta\,i}\;\mathrm{d}\lambda_i \tag{14}$$

where the $\mathrm{d}\lambda_i$ are parametrized by t':

$$\mathrm{d}\lambda_i = \frac{\mathrm{d}\lambda_i}{\mathrm{d}t'}\mathrm{d}t'$$

and the time evolution is replaced by a circuit in parameter space. Equation (12) is then replaced by:

$$K(t) = \mathcal{P}\exp\left\{i\int_{\mathrm{C}}\sum_i \tilde{A}'_{\eta\,i}\;\mathrm{d}\lambda_i\right\} \tag{15}$$

where $\mathcal{P}$ is an ordering operator along the circuit C.

The $\tilde{A}'_{\eta\,i}$ are identical with the gauge potentials introduced by Berry for the non-degenerate states [2], and by Wilczek and Zee for degenerate states [4].

The change-of-representation formalism then constitutes but a variant of the derivation of geometric phases, where one separates the phase production, through the effect of the gauge potentials on the eigenstates of the initial Hamiltonian $\mathcal{H}(0)$, and the change of eigenstates in Hilbert space, through the unitary operator $U_0(t)$ (although $U_0(t)$ does also contribute to the geometric phase production). The use of this formalism is not intended to prove anything new, but to make quantitative derivations easier in specific applications. For practical calculations, it is easier to use gauges depending on only one parameter, t, rather than to use as many gauges as there are parameters λ_i.

In a pulsed magnetic resonance experiment, one is interested in the expectation value of a quantity Q, starting from an initial density matrix $\rho(0)$:

$$\begin{aligned}\langle Q\rangle\,(t) &= \mathrm{Tr}\{QU(t)\rho(0)U^\dagger(t)\}\\ &= \mathrm{Tr}\left\{QU_0\tilde{U}\rho(0)\tilde{U}^\dagger U_0^\dagger\right\}.\end{aligned} \tag{16}$$

It is often simpler to use the equivalent expression:

$$\langle Q\rangle\,(t) = \mathrm{Tr}\left\{\left(U_0^\dagger Q U_0\right)\left(\tilde{U}\rho(0)\tilde{U}^\dagger\right)\right\} \tag{17}$$

and to calculate separately $U_0^\dagger Q U_0$ and $\tilde{U}\rho(0)\tilde{U}^\dagger$. It is this approach that will mostly be used in the following.

3 EPR on a rotating sample

3.1 General introduction

For reasons of simplicity and tractability, the discussion will be limited to pure J multiplets of rare-earth ions. In these ions at low concentration in a solid the magnetism arises from 4f electrons, and the hierarchy in the magnitude of the various interactions allows the use of the following perturbation scheme [23]:

- the Coulomb interaction between f electrons, combined with the Pauli principle, splits the ionic configuration into various terms L, S,
- the spin-orbit coupling, of the form $\Lambda\mathbf{L}\cdot\mathbf{S}$ within each term, splits the latter into various multiplets $J\,(\mathbf{J} = \mathbf{L} + \mathbf{S})\,,$
- the crystal field splits each multiplet into manifolds corresponding to irreducible representations of its symmetry group,
- the Zeeman interaction with an external field splits the degenerate manifolds. It is on such manifolds that one observes EPR.

This description is often very good, but sometimes, especially for heavy nuclei, it is insufficient, and one has *e.g.* an admixture of different J multiplets in a given crystal field manifold. We will neglect such admixtures and consider as an example the ground doublet of a J multiplet.

In the absence of an applied magnetic field, and with a sample rotation of frequency Ω around an axis Oz, the Hamiltonian within the J multiplet reduces to the time-dependent crystal field $V(t)$. Within this multiplet, V can be expressed in the form of a function of the components of the operator $\mathbf{J}$, according to the Wigner–Eckart theorem. It will have three orthogonal principal axes. The variation of $V(t)$ simply results from the rotation of these principal axes. We have then:

$$V(t) = \exp\left(-i\Omega J_z t\right)V_0\exp\left(i\Omega J_z t\right) \tag{18}$$

where V_0 is the *static* crystal field at initial time. This corresponds in equations (2, 4), to:

$$\begin{cases}U_0 &= \exp\left(-i\Omega J_z t\right)\\ A &= \Omega J_z.\end{cases} \tag{19}$$

If we are interested in measuring the magnetization along Ox, which is proportional to J_x:

$$\mu_x = -g_J\beta J_x \tag{20}$$

where g_J is the Landé g factor, and β the Bohr magneton, it is sufficient to look for the expectation value $\langle J_x\rangle$. Following equation (17), we have:

$$\begin{aligned}U_0^\dagger J_x U_0 &= \exp\left(i\Omega J_z t\right)J_x\exp\left(-i\Omega J_z t\right)\\ &= J_x\cos\Omega t - J_y\sin\Omega t.\end{aligned} \tag{21}$$

As for the effective Hamiltonian describing the evolution of $\tilde{U}(t)$, it is according to equations (11, 19):

$$\mathcal{H}_{\text{eff}} = V_0 - \Omega J_z. \tag{22}$$

Let us focus on the ground doublet. It can be described by a fictitious spin 1/2 S, with the following projections:

$$\begin{cases}J_X \to \xi_X S_X\\ J_Y \to \xi_Y S_Y\\ J_Z \to \xi_Z S_Z\end{cases} \tag{23}$$

where X, Y, Z are the principal axes of the crystal field. Let the cosines of x, y, z with respect to X, Y, Z be:

$$\begin{aligned}&\text{for } \mathrm{O}z : \lambda_X, \lambda_Y, \lambda_Z\\&\text{for } \mathrm{O}x : \mu_X, \mu_Y, \mu_Z\\&\text{for } \mathrm{O}y : \nu_X, \nu_Y, \nu_Z.\end{aligned} \tag{24}$$

In the space of the fictitious spin S, the crystal field V_0 reduces to a constant which can be ignored, and the effective Hamiltonian governing the evolution of the system is:

$$\mathcal{H}'_{\text{eff}} = -\Omega\left(\lambda_X \xi_X S_X + \lambda_Y \xi_Y S_Y + \lambda_Z \xi_Z S_Z\right). \tag{25}$$

As for the projection of $U_0^\dagger J_x U_0$ onto this doublet, it is:

$$\begin{aligned}\left(U_0^\dagger J_x U_0\right)' = {}&\left(\mu_X \xi_X S_X + \mu_Y \xi_Y S_Y + \mu_Z \xi_Z S_Z\right)\cos \Omega t\\&- \left(\nu_X \xi_X S_X + \nu_Y \xi_Y S_Y + \nu_Z \xi_Z S_Z\right)\sin \Omega t.\end{aligned} \tag{26}$$

The advantage of using the form (17) is that both $U_0^\dagger J_x U_0$ and $\mathcal{H}_{\text{eff}}$ are *linear* functions of the spin J components, which makes it possible to use the projection (23). If we had wanted to calculate $U_0 \tilde{U} \rho(0) \tilde{U}^\dagger U_0^\dagger$, the projection of the non-linear operator $U_0 = \exp\left(-i\Omega J_z t\right)$ onto the ground multiplet would have required a much more elaborate calculation.

The case when no external field is applied is of limited practical interest, because all states of each multiplet are equally populated at thermal equilibrium, so that no resonance experiment could be performed within any of them.

We will then consider the case of resonance in the presence of both a steady magnetic field and a sample rotation. We suppose that the rotation frequency is much smaller than the Zeeman coupling, itself much smaller than the crystal field splittings.

3.2 EPR pulse method

Most studies on paramagnetic rare earth ions, where J is a good quantum number, were performed under conditions where the g tensor of the ground doublet is axially symmetric, with principal values $g_\parallel$ and $g_\perp$, or even isotropic with a single g value. This corresponds to axial or isotropic projections of $\mathbf{J}$ onto the fictitious spin $\mathbf{S}$.

In order to avoid pointless complications (whose theoretical description would cause no problem) we limit ourselves to the case when the external field and the rotation axis are both parallel to a principal axis of the crystal field, say OZ. In the present section, we take the axis OZ parallel to the symmetry axis, which simplifies the discussion.

The modifications brought about to the preceding treatment are the following.

– Hamiltonian in the J multiplet:

$$\mathcal{H}(t) = g_J \beta B J_Z + \exp\left(-i\Omega J_Z t\right) V_0 \exp\left(i\Omega J_Z t\right) \tag{27}$$

where g_J is given by the Landé formula:

$$g_J = \frac{3}{2} + \frac{S\left(S+1\right) - L\left(L+1\right)}{2J\left(J+1\right)}, \tag{28}$$

where we have neglected $g-2$ for the electronic spins.

– Effective Hamiltonian for $\tilde{U}$:

$$\mathcal{H}_{\text{eff}} = \left(g_J \beta B - \Omega\right) J_Z + V_0. \tag{29}$$

– Effective Hamiltonian for the ground doublet:

$$\mathcal{H}'_{\text{eff}} = \left(g_J \beta B - \Omega\right) \xi_\parallel S_Z. \tag{30}$$

In this doublet, we have:

$$g_J \xi_\parallel = g_\parallel \tag{31}$$

$$g_J \xi_\parallel \beta B = \omega_{\text{e}}, \tag{32}$$

the Larmor frequency, and $\mathcal{H}'_{\text{eff}}$ can be written:

$$\mathcal{H}'_{\text{eff}} = \left(\omega_{\text{e}} - \xi_\parallel \Omega\right) S_Z = \left(\omega_{\text{e}} - \frac{g_\parallel}{g_J}\Omega\right) S_Z. \tag{33}$$

– Projection of $U_0^\dagger J_x U_0$ onto the ground multiplet:

Since in the present case, we have:

$$\xi_X = \xi_Y = \xi_\perp \tag{34}$$

all transverse directions are equivalent principal axes of the ground doublet g tensor, and we may choose the initial orientation Ox to be the principal axis OX. Equation (26) then yields:

$$\left(U_0^\dagger J_X U_0\right)' = \xi_\perp \left(S_X \cos \Omega t - S_Y \sin \Omega t\right) \tag{35}$$

which can be written:

$$\left(U_0^\dagger J_X U_0\right)' = \xi_\perp \exp\left(i S_Z \Omega t\right) S_X \exp\left(-i S_Z \Omega t\right). \tag{36}$$

Starting from thermal equilibrium, let us apply a microwave pulse at the Larmor frequency ω_{e} of the fictitious spin S, which will result in transverse spin components for $\rho(0)$ *in the ground doublet only.* In the interaction representation the rest of the evolution takes place in that doublet, that is, we must replace in equation (17):

$$\tilde{U} \rho(0) \tilde{U}^\dagger \quad \text{by} \quad \tilde{U}' \rho'(0) \tilde{U}'^\dagger$$

where $\rho'(0)$ is the projection of $\rho(0)$ on the ground doublet, and $\tilde{U}'$ is defined by:

$$\frac{\mathrm{d}}{\mathrm{d}t}\tilde{U}' = -i\mathcal{H}'_{\text{eff}} \tilde{U}' \tag{37}$$

that is, according to equation (33):

$$\tilde{U}' = \exp\left\{-i\left(\omega_{\text{e}} - \xi_\parallel \Omega\right) S_Z t\right\}. \tag{38}$$

We obtain, from (17, 36, 38):

$$\begin{aligned}\langle J_x\rangle(t) &= \mathrm{Tr}\left\{\tilde{U}'^{\dagger}\left(U_0^{\dagger}J_xU_0\right)'\tilde{U}'\rho'(0)\right\}\\ &= \xi_{\perp}\mathrm{Tr}\left\{\left(S_X\ \cos[\omega_{\mathrm{e}}-(\xi_{\|}-1)\Omega]t\right.\right.\\ &\qquad \left.\left.-\,S_Y\ \sin[\omega_{\mathrm{e}}-(\xi_{\|}-1)\Omega]t\right)\times\rho'(0)\right\}. \qquad (39)\end{aligned}$$

The final result is that the sample rotation results in a frequency shift:

$$\Delta\omega = -(\xi_{\|}-1)\Omega = -\left(\frac{g_{\|}}{g_J}-1\right)\Omega \qquad (40)$$

where the gauge potential $A=\Omega J_Z$ contributes to $-\xi_{\|}\Omega$, and the operator $U_0(t)$ to $+\Omega$.

It is appropriate to comment on the fundamental difference between the present problem and earlier NMR studies of Berry phases. Consider for instance the case of an axial quadrupole interaction [12,14,16]. In the course of a sample rotation, the circuit in parameter space is determined by the time variation of the polar angles θ and φ of the symmetry axis orientation. In particular, a rotation around this symmetry axis has no influence on the resonance spectrum (Except when using a properly designed geometry for the resonance excitation-detection device [24], which has nothing to do with the properties of the sample itself). In the present case of EPR, rotation around the symmetry axis *does* have a substantial effect: the frequency shift (40). Even though all axes normal to a symmetry axis are equivalent principal axes of the g tensor, it is necessary to choose arbitrarily two of them at initial time and to follow their evolution together with that of the third one, that is keep the three Euler angles. The reason for this difference is that the nuclear quadrupole Hamiltonian is expressed in the full Hilbert space of the nuclear spin, whereas the space of a crystal field doublet involves but a fraction of the $2J+1$ dimensional Hilbert space of the J multiplet, and it "wanders" through this space upon sample rotation.

On the experimental side, sample spinning in widely used in NMR for Magic Angle Spinning, with rotor frequencies of a few tens of kHz. As seen later, the ratios $|g_{\|}/g_J|$ are a few units, and the predicted frequency shift is of the order of several tens of kHz. This is much smaller than usual EPR linewidths. Although it might be observable in a pulse experiment, it might be more convenient to use the CW method, which makes use of a continuous mw irradiation of small amplitude together with lock-in detection of the absorption signal [25]. The information obtained by both methods is the same, since it is known from linear response that the CW signal is the Fourier transform of the FID signal following a pulse [26]. Another motivation for using CW is that there is no reason to limit oneself to rotation around the symmetry axis. As shown below, rotation around a different principal axis give rise to two shifts, but since both are much smaller than the EPR linewidth, what one would observe by CW is a weighted average of these shifts. Calculating this average requires the knowledge of the relative intensities of the two lines, which the present treatment is ill-adapted to determining, if only because the FID depends on the orientation of the mw field with respect to the principal axes at the time of the pulse. This is why we now analyze the CW observation of EPR.

3.3 The CW method

The initial Hamiltonian is now:

$$\mathcal{H}(t) = g_J\beta BJ_Z + g_J\,\beta B_1J_x\cos\omega t + V(t) \qquad (41)$$

and we look for the expectation value of $\langle J_x\rangle$, starting from an initial thermal equilibrium density matrix. We use the same interaction representation as in the preceding Section, and we project all operators on the ground doublet.

We still consider a sample rotation around the principal axis OZ, but we distinguish the three projections ξ_X, ξ_Y, ξ_Z, where two or three of them will eventually be equal. Let at initial time J_x be oriented at an angle φ from OX, in the OXY plane. This corresponds, in equation (24), to:

$$\mu_X = \nu_Y = \cos\varphi,$$
$$\mu_Y = -\nu_X = \sin\varphi$$

and equation (26) yields:

$$\begin{aligned}\left(U_0^{\dagger}J_xU_0\right)' &= (\xi_X\cos\varphi\,S_X+\xi_Y\sin\varphi\,S_Y)\cos\Omega t\\ &\quad + (\xi_X\sin\varphi\,S_X-\xi_Y\cos\varphi\,S_Y)\sin\Omega t. \qquad (42)\end{aligned}$$

It corresponds to an elliptical periodic motion. Through a little algebra, it can be written

$$\begin{aligned}\left(U_0^{\dagger}J_xU_0\right)' &= \frac{1}{2}(\xi_X+\xi_Y)\exp\left\{iS_Z(\Omega t-\varphi)\right\}S_X\\ &\quad\times\exp\left\{-iS_Z(\Omega t-\varphi)\right\}+\frac{1}{2}(\xi_X-\xi_Y)\\ &\quad\times\exp\left\{-iS_Z(\Omega t-\varphi)\right\}S_X\exp\left\{iS_Z(\Omega t-\varphi)\right\}. \qquad (43)\end{aligned}$$

As for the effective Hamiltonian, it is:

$$\mathcal{H}'_{\mathrm{eff}} = (\omega_{\mathrm{e}}-\xi_Z\Omega)\,S_Z+\omega_1\left(U_0^{\dagger}J_xU_0\right)'\cos\omega t \qquad (44)$$

where we have written $g_J\beta B_1=\omega_1$.

Let us consider the contribution to $\langle J_x\rangle$ of the first term on the right-hand side of equation (43):

$$\begin{aligned}\langle J_x\rangle_1 &= \frac{1}{2}(\xi_X+\xi_Y)\,\mathrm{Tr}\left\{\exp\left[iS_Z(\Omega t-\varphi)\right]S_X\right.\\ &\quad\left.\times\exp\left[-iS_Z(\Omega t-\varphi)\right]\times\tilde{U}'\rho(0)\tilde{U}'^{\dagger}\right\} \qquad (45)\end{aligned}$$

which can be written:

$$\begin{aligned}\langle J_x\rangle_1 &= \frac{1}{2}(\xi_X+\xi_Y)\,\mathrm{Tr}\left\{S_X\exp\left[-iS_Z(\Omega t-\varphi)\right]\right.\\ &\quad\left.\times\,\tilde{U}'\rho(0)\tilde{U}'^{\dagger}\exp\left[iS_Z(\Omega t-\varphi)\right]\right\}. \qquad (46)\end{aligned}$$

The evolution of the operator:

$$\exp\left[-iS_Z\left(\Omega t-\varphi\right)\right]\tilde{U}'$$

is determined by a new effective Hamiltonian:

$$\begin{aligned}\mathcal{H}'_{\mathrm{eff}_1} &= \left[\omega_{\mathrm{e}}-\left(\xi_Z-1\right)\Omega\right]S_Z+\omega_1\cos\omega t\\ &\times\left\{\frac{1}{2}\left(\xi_X+\xi_Y\right)S_X++\frac{1}{2}\left(\xi_X-\xi_Y\right)\right.\\ &\times\left.\exp\left[-i2S_Z\left(\Omega t-\varphi\right)\right]S_X\exp\left[i2S_Z\left(\Omega t-\varphi\right)\right]\right\}.\end{aligned} \tag{47}$$

To proceed, we add relaxation terms for $\langle S_X\rangle$, $\langle S_Y\rangle$ and $\langle S_Z\rangle$. This gives rise to Bloch equations in the laboratory frame [27], and the CW signal is obtained from their asymptotic solution. This solution does not depend on the exact time when the small mw field is applied, that is on the initial angle φ between J_x and J_X. We may therefore take the average over φ of the excitation. The last term on the right-hand side of equation (47), equal to:

$$S_X\cos 2\left(\Omega t-\varphi\right)+S_Y\sin 2\left(\Omega t-\varphi\right)$$

has a vanishing average. The final result is that the first contribution to the CW response is a resonance signal shifted by:

$$\Delta\omega_1=-\left(\xi_Z-1\right)\Omega, \tag{48}$$

of relative amplitude:

$$A_1\propto\left(\xi_X+\xi_Y\right)^2. \tag{49}$$

The contribution $\langle J_x\rangle_2$ from the second term on the right-hand side of equation (43) is determined in a similar way. It is a resonance signal shifted by:

$$\Delta\omega_2=-\left(\xi_Z+1\right)\Omega \tag{50}$$

of relative amplitude:

$$A_2\propto\left(\xi_X-\xi_Y\right)^2. \tag{51}$$

The average shift is then:

$$\Delta\omega=-\left(\frac{g_Z}{g_J}-\lambda\right)\Omega \tag{52}$$

with:

$$\lambda=\frac{A_1-A_2}{A_1+A_2}=\frac{2\xi_X\xi_Y}{\xi_X^2+\xi_Y^2}=\frac{2g_Xg_Y}{g_X^2+g_Y^2} \tag{53}$$

where we have generalized the relation (31) to the axes X and Y.

In the axial case, when $g_X=g_Y, \lambda$ is equal to unity, and equation (52) reduces to (40).

These conclusions are not modified if the resonance linewidth is determined by static mechanisms, such as a distribution of g values due to the sample mosaicity, or superhyperfine interactions. One then uses Bloch equations for each spin packet, and the shift of the inhomogeneously broadened line is still given by equations (52, 53).

The frequency shift (52) is an algebraic quantity which adds to the Larmor frequency ω_{e} of sign equal to that of g_Z. What one would observe experimentally is the shift in the absolute value of the resonance frequency, that is:

$$\frac{\Delta\omega_{\mathrm{obs.}}}{\Omega}=\frac{g_Z}{|g_Z|}\frac{\Delta\omega}{\Omega}$$

or else, according to equation (52):

$$\Delta\omega_{\mathrm{obs.}}=-\left(\frac{|g_Z|}{g_J}-\frac{g_Z}{|g_Z|}\lambda\right)\Omega. \tag{54}$$

We have constantly referred to the crystal field ground multiplet of the J multiplet. It is evident that the theory applies to any multiplet, provided the temperature is high enough for it to be sizeably populated.

Examples for rare-earth ions

We have selected ions for which the picture where L, S, J are good quantum numbers is approximately valid and where the ratios $\Delta\omega/\Omega$ are substantial. The quoted figures should be accurate to within a few per cent. All g tensors are axially symmetric or isotropic. The background information is from reference [23].

Some of the nuclei have spin, and the EPR spectrum consists of a hyperfine multiplet. The frequency shift is the same for all lines.

1) Ce^{3+} in $LaCl_3$, ground doublet. State $^2F_{5/2}(S=1/2, L=3, J=5/2)$. $g_J=6/7$
   $g_\parallel\simeq-4.037,\qquad g_\perp\simeq-0.17$
   OZ parallel to symmetry axis: $\lambda=1$.

$$\Delta\omega_{\mathrm{obs.}}/\Omega=-5.71. \tag{55}$$

2) Nd^{3+} in $LaCl_3$, ground doublet. State $^4I_{9/2}(S=3/2, L=6, J=9/2)$.
   $g_J=8/11$
   $g_\parallel\simeq 4,\qquad g_\perp\simeq 1.76$
   OZ parallel to symmetry axis: $\lambda=1$.

$$\Delta\omega_{\mathrm{obs.}}/\Omega=-4.50. \tag{56}$$

3) Dy^{3+} in yttrium ethylsulphate $Y\left(C_2H_5SO_4\right)_3, 9H_2O$. Excited doublet at $\sim 15\ \mathrm{cm}^{-1}$. State $^6H_{15/2}(S=5/2, L=5, J=15/2)$.
   $g_J=4/3$
   $g_\parallel\simeq 5.86,\qquad |g_\perp|\simeq 8.4$
   i) OZ parallel to symmetry axis: $\lambda=1$

$$\Delta\omega_{\mathrm{obs}}/\Omega=-3.40. \tag{57}$$

   ii) OZ perpendicular to symmetry axis:

$$g_Z=g_\perp, g_X=g_\parallel, g_Y=g_\perp.$$

Since λ is proportional to $g_Y = g_Z = g_\perp$ (Eq. (53)), the observed shift is according to equation (54), independent of the sign of $g_\perp$. We have:

$$|\lambda| = 0.94, \qquad \Delta\omega_{\text{obs}}/\Omega = -5.36. \tag{58}$$

4) Dy^{3+}in La Mg double nitrate (LMN), La_2 Mg_3 $(N0_3)_{12}$, $24H_20$. Ground doublet. Same S, L, J, g_J as above. $g_\parallel \simeq 4.28$, $|g_\perp| \simeq 8.92$
   i) OZ parallel to symmetry axis:

$$\Delta\omega_{\text{obs}}/\Omega = -2.28. \tag{59}$$

   ii) OZ perpendicular to symmetry axis:

$$|\lambda| = 0.78 \qquad \Delta\omega_{\text{obs}}/\Omega = -5.91. \tag{60}$$

5) Ho^{2+} in CaF_2, ground doublet. State $^4I_{15/2}(S=3/2, L=6, J=15/2)$.
$g_J = 6/5$
$g \simeq -5.91$ (isotropic)

$$\Delta\omega_{\text{obs}}/\Omega = -5.93. \tag{61}$$

6) Er^{3+} in CaF_2, ground doublet. Same state as for Ho^{2+}, and same g_J.
$g \simeq +6.78$

$$\Delta\omega_{\text{obs}}/\Omega = -4.65. \tag{62}$$

The main difference with Ho^{2+} is in the sign of g for the ground doublet. According to equation (54), we have:

$$\begin{aligned}\frac{\Delta\omega_{\text{obs}}}{\Omega} &= -\left(\frac{|g_Z|}{g_J} - 1\right) \quad \text{for } g_Z > 0\\ &= -\left(\frac{|g_Z|}{g_J} + 1\right) \quad \text{for } g_Z < 0.\end{aligned}$$

Had the g signs been opposite, the expected shifts would have been:

$$\begin{cases} \text{“}(\Delta\omega_{\text{obs}}/\Omega)\text{”}\left(Ho^{2+}\right) = -3.93\\ \text{“}(\Delta\omega_{\text{obs}}/\Omega)\text{”}\left(Er^{3+}\right) = -6.65. \end{cases} \tag{63}$$

4 Conclusion

As stated in the Introduction, the main purpose of this article was to predict the outcome of well-defined experiments: the EPR resonance shift in a crystal field doublet resulting from sample spinning. The theory was developed along the standard procedure in magnetic resonance: the use of an interaction representation.

For simplicity, the theory only considered crystal field doublets in a pure J multiplet, with magnetic field and rotation axis both parallel to a crystal field principal axis. It is formally easy to extend it to more general cases, at the price of more complex calculations.

Besides offering an original illustration of geometric phases, the observation of the frequency shift in rotating samples might provide information of some use on paramagnetic ions in solids. The most obvious one is that of the sign of the $g_\parallel$ values. An example at hand is that of Ho^{2+} and Er^{3+} in CaF_2 (examples 5 and 6). Both ions have the same configuration $4f^{11}$, $^4I_{15/2}$. From theory, the nature of the ground doublet is very sensitive to the crystal field. It may be a doublet Γ_6, with theoretical $g = -6$, or Γ_7, with theoretical $g = +6.8$. The assignments have been made according to the proximity of the experimental $|g|$ to those values, assuming the departure from the L, S, J approximation to be small. EPR under rotation might settle the question: for g values of opposite signs the observed frequency shifts would be close to those of equation (63), rather than (61) and (62). There are several cases where the experimental g values point strongly towards a severe breaking of the L, S, J scheme. EPR under rotation might yield helpful information for such cases. However, it would be necessary in that case to express the eigenbasis of the fictitious spin S as a function of that of J, or L, S, or the ℓ_i, s_i of individual electrons, and the theory would be spoiled of its simplicity.

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Appendix A: Perturbation theory and parallel transport

The theory of geometric topological phases is closely connected to that of parallel transport in fiber bundles, a mathematical concept of differential geometry [7–9]. Its formalism is widely used in several branches of physics, such as non-Abelian gauge theories of elementary particles. We describe in this Appendix a simple and natural way of building a parallel transport through time-independent perturbation theory, on the example of an electronic crystal field doublet upon sample rotation.

Without entering into detailed mathematics, the definition of parallel transport in quantum mechanics goes as follows. Let $|\Phi(t)\rangle$ be a continuous, non degenerate eigenket of a periodic Hamiltonian $\mathcal{H}(t)$, subjected to the condition:

$$\left\langle \Phi(t) \middle| \frac{\mathrm{d}}{\mathrm{d}t}\Phi(t) \right\rangle = 0. \tag{A.1}$$

The circuit followed by $|\Phi(t)\rangle$ in parameter space corresponds to a parallel transport. One can show that, after a full cycle of evolution of $\mathcal{H}(t)$, one has:

$$|\Phi(T)\rangle = \exp(i\gamma)|\Phi(0)\rangle \tag{A.2}$$

where γ is equal to Berry's phase.

We consider as in Section 3 a magnetic field and rotation axis parallel to the principal axis OZ.

Let us consider an eigenstate $|m_G(\varphi)\rangle$ of the projection of J_Z on the ground multiplet, when the sample has been rotated by an angle φ from its initial orientation, and the corresponding eigenstate $|m_G(\varphi+\mathrm{d}\varphi)\rangle$ after an extra rotation by dφ. According to equation (27), the new crystal field is (with $\varphi = \Omega t$):

$$V(\varphi+\mathrm{d}\varphi) = V(\varphi) - i\mathrm{d}\varphi\,[J_Z, V(\varphi)] \tag{A.3}$$

from which we can determine $|m_G(\varphi+\mathrm{d}\varphi)\rangle$ by first-order perturbation:

$$\begin{aligned}|m_G(\varphi+\mathrm{d}\varphi)\rangle &= |m_G(\varphi)\rangle \\ &\quad+\sum\frac{|n\rangle\langle n|-i\mathrm{d}\varphi[J_Z,V(\varphi)]|m_G(\varphi)\rangle}{E_{m_G}-E_n} \\ &= |m_G(\varphi)\rangle \\ &\quad- i\mathrm{d}\varphi\sum\frac{|n\rangle\langle n|(J_ZV(\varphi)-V(\varphi)J_Z)|m_G(\varphi)\rangle}{E_{m_G}-E_n}\,\cdot\end{aligned} \tag{A.4}$$

Since $V(\varphi)$ is a multiple of the unit operator within each crystal field multiplet, only those kets $|n\rangle$ belonging to other multiplets than the ground multiplet yield a non-vanishing contribution. If, as we assume, the Zeeman splitting is much smaller than the inter-multiplet splittings, we have:

$$\begin{cases} V(\varphi)\,|m_G(\varphi)\rangle \simeq E_{m_G}\,|m_G(\varphi)\rangle \\ \langle n|\,V(\varphi) \simeq E_n\,\langle n| \end{cases} \tag{A.5}$$

and equation (A.4), yields:

$$\begin{aligned}|m_G(\varphi+\mathrm{d}\varphi)\rangle - |m_G(\varphi)\rangle &= \mathrm{d}\,|m_G(\varphi)\rangle \\ &= -i\mathrm{d}\varphi\sum{}'\,|n\rangle\,\langle n|\,J_Z\,|m_G(\varphi)\rangle\end{aligned} \tag{A.6}$$

where the sum is restricted to kets $|n\rangle$ outside the ground multiplet. We have then:

$$\langle m_G(\varphi)|\,\mathrm{d}\,|m_G(\varphi)\rangle = 0 \tag{A.7}$$

so that the evolution (A.4) or (A.6) of $|m_G(\varphi)\rangle$ corresponds to a parallel transport on the fiber bundle describing the ground doublet.

This procedure for building a parallel transport is in fact general. It can be used with the operator $\mathcal{H}(t)$ of equations (2, 4), from which:

$$\mathrm{d}\mathcal{H}(t) = -i\mathrm{d}t\,[A(t), \mathcal{H}(t)]$$

where we have ignored the variation of $\mathcal{H}_0(t)$, which does not modify the eigenstates.

Let us consider the ground doublet subspace $G(0)$ for the crystal field $V(0)$, and the subspace $G(\varphi)$, obtained by parallel transport throughout the rotation by the angle φ. One can define a fictitious spin within each doublet, but there is no obvious connection between them since the subspaces of the J Hilbert space on which they act are different. Our next task is to establish a connection between bases for each doublet, and between the matrices in these bases of the projection of an operator J_α on $G(0)$ and $G(\varphi)$.

We call:

$$\mathcal{P}_G(\varphi) = \sum\nolimits_G |m'_G(\varphi)\rangle\,\langle m'_G(\varphi)| \tag{A.8}$$

the projection operator on the ground doublet $G(\varphi)$. We have:

$$\sum{}'\,|n\rangle\,\langle n| = 1 - \mathcal{P}_G(\varphi) \tag{A.9}$$

and equations (A.4, A.6) yield:

$$|m_G(\varphi+\mathrm{d}\varphi)\rangle = [1 - i\mathrm{d}\varphi(1-\mathcal{P}_G(\varphi))J_Z]\,|m_G(\varphi)\rangle\,. \tag{A.10}$$

Let us now consider the projection of an operator J_α on the doublet $G(\varphi+\mathrm{d}\varphi)$. According to equation (A.10), we have, to first order in dφ:

$$\begin{aligned}&\langle m'_G(\varphi+\mathrm{d}\varphi)|J_\alpha|m_G(\varphi+\mathrm{d}\varphi)\rangle \\ &\quad=\langle m'_G(\varphi)|[1+i\mathrm{d}\varphi J_Z(1-\mathcal{P}_G)]J_\alpha \\ &\qquad\times[1-i\mathrm{d}\varphi(1-\mathcal{P}_G)J_Z]|m_G(\varphi)\rangle \\ &\quad=\langle m'_G(\varphi)|J_\alpha|m_G(\varphi)\rangle + i\mathrm{d}\varphi\langle m'_G(\varphi)|\{[J_Z,J_\alpha] \\ &\qquad-(J_Z\mathcal{P}_G(\varphi)J_\alpha - J_\alpha\mathcal{P}_G(\varphi)J_Z)\}|m_G(\varphi)\rangle\end{aligned} \tag{A.11}$$

which may be written more generally:

$$\begin{aligned}&\mathcal{P}_G(\varphi+\mathrm{d}\varphi)J_\alpha\mathcal{P}_G(\varphi+\mathrm{d}\varphi) \\ &\quad= \mathcal{P}_G(\varphi)J_\alpha\mathcal{P}_G(\varphi) + i\mathrm{d}\varphi\,\{\mathcal{P}_G(\varphi)[J_Z,J_\alpha]\mathcal{P}_G(\varphi) \\ &\qquad-[\mathcal{P}_G(\varphi)J_Z\mathcal{P}_G(\varphi),\mathcal{P}_G(\varphi)J_\alpha\mathcal{P}_G(\varphi)]\}\,.\end{aligned} \tag{A.12}$$

For $J_\alpha = J_Z$, we obtain:

$$\mathcal{P}_G(\varphi+\mathrm{d}\varphi)J_Z\mathcal{P}_G(\varphi+\mathrm{d}\varphi) = \mathcal{P}_G(\varphi)J_Z\mathcal{P}_G(\varphi). \tag{A.13}$$

The matrix of J_Z does not vary during the parallel transport, and we may choose as a connected basis the eigenkets of J_Z in each doublet $G(\varphi)$.

Let X, Y, Z be the crystal field principal axes for the orientation φ. The connection between $J_{X,Y,Z}$ and the fictitious spin components $S_{X,Y,Z}$ for this orientation is given by equation (23).

We obtain then, from equation (A.12):

$$\begin{aligned}\mathcal{P}_G(\varphi+\mathrm{d}\varphi)J_X\mathcal{P}_G(\varphi+\mathrm{d}\varphi) &= \xi_XS_X + i\mathrm{d}\varphi\{\mathcal{P}_G(\varphi)iJ_Y\mathcal{P}_G(\varphi) \\ &\quad-[\xi_ZS_Z,\xi_XS_X]\} = \xi_XS_X + \mathrm{d}\varphi(\xi_Z\xi_X-\xi_Y)S_Y\end{aligned} \tag{A.14}$$

and likewise:

$$\mathcal{P}_G(\varphi+\mathrm{d}\varphi)J_Y\mathcal{P}_G(\varphi+\mathrm{d}\varphi) = \xi_YS_Y - \mathrm{d}\varphi(\xi_Z\xi_Y-\xi_X)S_X. \tag{A.15}$$

We introduce the following notations. We call $J_{X,Y,Z}(\varphi)$ the J operators along the principal axes

$X, Y, Z\,(\varphi)$ corresponding to the orientation φ. The operators in equations (A.14) and (A.15) are $J_{X,Y}\,(\varphi)$. We call $\tilde{S}_{X,Y,Z}\,(\varphi)$ the matrices in the above defined connected bases of the fictitious spin components in $G\,(\varphi)$ along the principal axes $X, Y, Z\,(\varphi)$. After a rotation of angle $\mathrm{d}\varphi$, we have:

$$J_X\,(\varphi + \mathrm{d}\varphi) = J_X\,(\varphi) + \mathrm{d}\varphi J_Y\,(\varphi) \qquad (\text{A.16})$$
$$J_Y\,(\varphi + \mathrm{d}\varphi) = J_Y\,(\varphi) - \mathrm{d}\varphi J_X\,(\varphi)\,. \qquad (\text{A.17})$$

Inserting these forms into equations (A.14, A.15), we obtain:

$$\begin{cases} \tilde{S}_X\,(\varphi + \mathrm{d}\varphi) = \tilde{S}_X\,(\varphi) + \mathrm{d}\varphi \xi_Z \tilde{S}_Y\,(\varphi) \\ \tilde{S}_Y\,(\varphi + \mathrm{d}\varphi) = \tilde{S}_Y\,(\varphi) - \mathrm{d}\varphi \xi_Z \tilde{S}_X\,(\varphi) \end{cases} \qquad (\text{A.18})$$

which can be written in differential form:

$$\begin{cases} \dfrac{\mathrm{d}}{\mathrm{d}\varphi}\tilde{S}_X\,(\varphi) = \xi_Z \tilde{S}_Y\,(\varphi) \\[2ex] \dfrac{\mathrm{d}}{\mathrm{d}\varphi}\tilde{S}_Y\,(\varphi) = -\xi_Z \tilde{S}_X\,(\varphi)\,. \end{cases} \qquad (\text{A.19})$$

It is because we end up with differential equations that it is sufficient to use first order perturbation in equations (A.6−A.11).

We obtain upon integration:

$$\begin{cases} \tilde{S}_X\,(\varphi) = \tilde{S}_X(0)\cos(\xi_Z\varphi) + \tilde{S}_Y(0)\sin(\xi_Z\varphi) \\ \tilde{S}_Y\,(\varphi) = \tilde{S}_Y(0)\cos(\xi_Z\varphi) - \tilde{S}_X(0)\sin(\xi_Z\varphi)\,. \end{cases} \qquad (\text{A.20})$$

Let us now follow the projection on $G\,(\varphi)$ of a constant operator: $J_x = J_X(0)$, which is equal to:

$$J_X(0) = J_X\,(\varphi)\cos\varphi - J_Y\,(\varphi)\sin\varphi. \qquad (\text{A.21})$$

This projection is:

$$\xi_X \tilde{S}_X\,(\varphi)\cos\varphi - \xi_Y \tilde{S}_Y\,(\varphi)\sin\varphi$$

whence, according to equations (A.20):

$$\begin{aligned} \mathcal{P}(\varphi) J_x \mathcal{P}(\varphi) = {} & \tilde{S}_X(0)(\xi_X\cos\varphi\cos(\xi_Z\varphi) \\ & + \xi_Y \sin\varphi\sin(\xi_Z\varphi)) \\ & + \tilde{S}_Y(0)(\xi_X\cos\varphi\sin(\xi_Z\varphi) \\ & - \xi_Y\sin\varphi\cos(\xi_Z\varphi)). \end{aligned} \qquad (\text{A.22})$$

If we choose, for the initial orientation, $\langle m'_G(0)|\,\tilde{S}_X(0)\,|m_G\,(0)\rangle = 1/2$, we obtain for the phase acquired by each eigenstate of J_Z in $G\,(\varphi)$:

$$|m_G\,(\varphi)\rangle = \exp\left[im\gamma\,(\varphi)\right]|m_G(0)\rangle \qquad (\text{A.23})$$

from the phase of:

$$\langle -_G\,(\varphi)|\,J_x\,|+_G\,(\varphi)\rangle = \lambda\,(\varphi)\exp\left[i\gamma\,(\varphi)\right] \qquad (\text{A.24})$$

where the modulus λ depends on φ if $\xi_X \neq \xi_Y$.

According to equation (A.22), we have:

$$\begin{aligned} \langle -_G(\varphi)|J_x|+_G\,(\varphi)\rangle = {} & \frac{1}{2}\{\xi_X\cos\varphi\cos(\xi_Z\varphi) \\ & + \xi_Y\sin\varphi\sin(\xi_Z\varphi) + i[\xi_X\cos\varphi\sin(\xi_Z\varphi) \\ & - \xi_Y\sin\varphi\cos(\xi_Z\varphi)]\} \end{aligned} \qquad (\text{A.25})$$

whence:

$$\tan\gamma\,(\varphi) = \frac{\tan(\xi_Z\varphi) - (\xi_Y/\xi_X)\tan\varphi}{1 + (\xi_Y/\xi_X)\tan\varphi\tan(\xi_Z\varphi)}\,\cdot \qquad (\text{A.26})$$

Or else, if we define a new angle φ' through:

$$\tan\varphi' = \frac{\xi_Y}{\xi_X}\tan\varphi \qquad (\text{A.27})$$

we obtain:

$$\gamma\,(\varphi) = \xi_Z\varphi - \varphi'. \qquad (\text{A.28})$$

The present procedure makes it possible to follow continuously the topological phase accumulated by the adiabatically invariant eigenkets of the Hamiltonian (Zeeman interaction along OZ) during a parallel transport.

Equation (A.26) simplifies for the axial case, when $\xi_Z = \xi_\parallel$ and $\xi_X = \xi_Y = \xi_\perp$. We obtain:

$$\gamma\,(\varphi) = \left(\xi_\parallel - 1\right)\varphi. \qquad (\text{A.29})$$

When $\xi_X \neq \xi_X$, equation (A.22) can be written:

$$\begin{aligned} \mathcal{P}\,(\varphi)\,J_x\mathcal{P}\,(\varphi) = {} & \frac{1}{2}\left(\xi_X + \xi_Y\right)\exp\left\{-i\left(\xi_Z - 1\right)\varphi S_Z\right\}S_X \\ & \times \exp\left\{i\left(\xi_Z - 1\right)\varphi S_Z\right\} \\ & + \frac{1}{2}\left(\xi_X - \xi_Y\right)\exp\left\{-i\left(\xi_Z + 1\right)\varphi S_Z\right\} \\ & \times S_X\exp\left\{i\left(\xi_Z + 1\right)\varphi S_Z\right\}. \end{aligned} \qquad (\text{A.30})$$

For a periodic rotation: $\varphi = \Omega t$, this last equation bears a strong analogy with the weighted frequency shifts predicted in CW EPR.

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