

Communication

The harmonic inversion of the field-swept fixed-frequency resonance spectrum

Claudio José Magon ^{*}, José Fernando Lima, Ronny Rocha Ribeiro, Mateus José Martins

Instituto de Física de São Carlos, Universidade de São Paulo, P.O. Box 369, 13560-970 São Carlos, SP, Brazil

Received 20 April 2006; revised 24 August 2006

Available online 20 October 2006

Abstract

When the spin Hamiltonian is a linear function of the magnetic field intensity the resonance fields can be determined, in principle, by an eigenfield equation. In this report, we show a new technical approach to the resonance field problem where the eigenfield equation leads to a dynamic equation or, more specifically, to a first order differential equation of a variable $L(x)$, where x is associated with the magnetic field h . Such differential equation has the property that: its stationary solution is the eigenfield equation and the spectral information contained in $L(x)$ is directly related to the resonance spectrum. Such procedure, known as the “harmonic inversion problem” (HIP), can be solved by the “filter diagonalization method” (FDM) providing sufficient precision and resolution for the spectral analysis of the dynamic signals. Some examples are shown where the resonance fields are precisely determined in a single procedure, without the need to solve eigenvalue equations.

© 2006 Elsevier Inc. All rights reserved.

Keywords: Eigenfields; Resonance fields; Simulation of the resonance spectrum; Harmonic inversion problem; HIP; Filter diagonalization method; FDM

1. Introduction

In most continuous-wave (cw) resonance experiments, also called field-swept experiments, a fixed frequency is maintained and the applied magnetic field strength is swept. Such arrangement means that a parameter of the spin Hamiltonian, the magnetic field in this case, is swept and for some specific values of this parameter a transition is observed. Actually, more than one transition can be simultaneously observed for a given value of the field. The fact that the time dependent excitation is frequency-fixed and the Hamiltonian varies during the measurement process brings up a technical difficulty for the establishment of an appropriate procedure to find the correct values of the magnetic field, usually called the *resonance fields*, for which the transitions may occur.

The above methodology is particularly employed in most electron paramagnetic resonance experiments (EPR), where one can extract magnetic parameters and then deduce structural and dynamical information about the paramagnetic molecules or other paramagnetic centers that are being measured. The numerical simulation of the EPR spectra is of fundamental importance, and for this purpose computers have been used extensively for decades. In this context, there are several software packages that are available for the simulation of the EPR spectrum. Some of them are commercial products and others can be obtained free of charge from the magnetic resonance community. We are familiar with two of them, the well-known program QPOWA (dedicated to $S = 1/2$ spin systems) [1,2] and the new software package EasySpin [3].

To simulate an EPR spectrum the first difficulty that arises is the assignment of all the resonance fields of a given spin Hamiltonian that are compatible with the energy of the radiating microwave field. There are several known algorithms that can be used for this purpose but, from

^{*} Corresponding author. Fax: +551633739876.

E-mail address: magon@ifsc.usp.br (C.J. Magon).

our knowledge, there is only one published procedure capable to determine all resonance fields by means of a direct calculation based on first principles [4]. Following this reference, the resonance field problem can be formulated and solved in an explicit form, however, as will be explained later, such approach is computationally too costly, even in nowadays, because of the n^2 dimension of the matrices involved, with n being the dimension of the spin Hamiltonian, therefore, its applicability is feasible only for small systems or on powerful computers. Approximation methods, usually based on perturbation theories either by using explicit formulas or by means of numerical treatment, are used extensively [5,6]. Extrapolative methods are based on frequency-shift perturbation theory, also called eigenfield perturbation theory [7]. Root-finding algorithms are based on the Newton–Raphson method and supplemented with the Muller method for bisection and quadratic interpolation [8]. Extrapolation and root-finding methods are reliable only on a narrow field range. Homotopy methods make use of a least-squares method [9] or Newton–Raphson steps combined with Rayleigh quotient iteration [10]. The method used in the software package EasySpin implement a new energy level modeling procedure based on iterative adaptive bisections [3].

Recently, a numerical procedure to compute eigenenergies of a possibly large quantum system using solutions of time-dependent equations, known as “filter diagonalization method”, or FDM, was introduced [11]. This method is being extensively used for the spectral analysis of time signals [12]. Inspired by the conceptual connections between the FDM and the resonance field problem, we are here for a re-visit to the eigenfield method introduced in reference [4].

In this work, we will focus our attention to the eigenfield method proposed in 1973 [4] and we will propose a new formulation for the resonance field problem based on a hypothesis that the eigenfield equation can give birth to a dynamic equation, more specifically, to a differential equation on a variable associated with the magnetic field. From the dynamic solutions of such equation, the resonance fields can be determined exactly without the need to directly solve eigenvalue equations. Such approach can only be accomplished with the FDM, which can provide sufficient precision and resolution for the spectral analysis of dynamic signals. We hope that by suggesting a new way to calculate resonance fields we are providing some insight into the essential structure of the problem.

2. Theory, results and discussion

Following an early work [4], an eigenfield equation is formulated in the Liouville space where the resonance field problem can be solved in an explicit form. In order to make our arguments accessible to a wider audience, we will repeat here—sometimes verbatim—a brief explanation of the basic assumptions of that work and some of its practical consequences.

The procedure assumes that the spin Hamiltonian, \mathbf{H} , is a linear function of the applied magnetic field strength h :

$$\mathbf{H}(h, \theta, \varphi) = \mathbf{F} + h\mathbf{G}(\theta, \varphi) \tag{1}$$

and

$$\vec{H} = h(\sin(\theta) \cos(\varphi), \sin(\theta) \sin(\varphi), \cos(\theta)) \tag{2}$$

Here, \mathbf{F} and \mathbf{G} are field-independent Hermitian operators, where \mathbf{G} carries the angular dependence of the magnetic field vector \vec{H} .

A transition produced by an excitation of frequency Ω may occur between two energy levels specified by:

$$\begin{aligned} \mathbf{H}|\omega_k\rangle &= \omega_k|\omega_k\rangle \\ \mathbf{H}|\omega_{k'}\rangle &= \omega_{k'}|\omega_{k'}\rangle = (\omega_k + \Omega)|\omega_{k'}\rangle, \quad k = 0, \dots, n-1 \end{aligned} \tag{3}$$

After some algebraic manipulation of this constraint, the energy ω_k can be eliminated from these equations, resulting:

$$\mathbf{H}|\omega_k\rangle\langle\omega_{k'}| - |\omega_k\rangle\langle\omega_{k'}|\mathbf{H} = \Omega|\omega_k\rangle\langle\omega_{k'}| \tag{4}$$

A particular set of basis functions, $|\alpha_i\rangle$, $i = 0, \dots, n-1$, that forms a complete basis is usually assumed:

$$|\omega_k\rangle = \sum_{i=0}^{n-1} a_{ik}|\alpha_i\rangle \tag{5}$$

Inserting the hypothesis formulated in Eq. (1) into Eq. (4), the following eigenvalue equation can be deduced (same as Eq. (5) of Ref. [4]):

$$(F - \Omega I)M - MF = h(MG - GM) \tag{6}$$

In this equation: the resonance field h is the eigenvalue; F , G , I and M are $n \times n$ matrices; M is the eigenmatrix and I is the identity matrix. In terms of the basis defined in Eq. (5) the matrix elements of M , F and G are, respectively:

$$\begin{aligned} M_{ij} &= a_{ik}a_{jk}^* \\ F_{ij} &= \langle\alpha_i|\mathbf{F}|\alpha_j\rangle \\ G_{ij} &= \langle\alpha_i|\mathbf{G}|\alpha_j\rangle \end{aligned} \tag{7}$$

Eq. (6) admits solutions for only certain values of h and the corresponding eigenmatrices will give all the information needed to calculate the associated transition moments.

If the matrix M is rewritten as a column vector, Z , of dimension $n^2 \times 1$, the Eq. (6) can be put in the form of a generalized eigenvalue equation (same as Eq. (6) of Ref. [4]):

$$AZ = hBZ \tag{8}$$

Here, A and B are $n^2 \times n^2$ matrices and the explicit form of the elements of A can be calculated from Ω and F , and those of B from G . In the original work this result is explored in a variety of situations but here we will discuss only some details that are relevant to this report.

First, A and B are Hermitian and, besides, if A is non-singular the generalized equation can be reduced to a ordinary eigenvalue problem:

$$CZ = (1/h)Z \tag{9}$$

The matrix $C = A^{-1}B$ is not Hermitian in general. Since one expect to solve (8) or (9) to obtain real eigenvalues (or real resonance fields), the positive-definiteness of matrices A and B must be taken into account. It can be proved that if A or B is positive-definite the eigenvalues, h (or $1/h$), are real, in which case there is a suitable transformation that brings matrix C to a Hermitian form; however, if neither A nor B is positive-definite some of the eigenvalues may be complex (see, for instance, Ref. [13], pp. 35–36, 337–343). This last situation connotes non-Hermitian Hamiltonians, therefore, only the real eigenvalues need to be found. The matrix B , which is calculated from G , is generally not positive-definite, but matrix A , which is calculated from Ω and F , is positive-definite if and only if all possible zero-field transitions energies are less than Ω . In general, each eigenvalue has a companion eigenvalue of equal magnitude but opposite sign and, if the eigenvalue is complex, its conjugate is also an eigenvalue. Therefore, real eigenvalues appear as pairs, $\pm\alpha$, and complex ones as quartets, $\pm\alpha \pm i\beta$, with α and β positive numbers of comparable magnitudes.

In principle, the above formulation of the resonance field problem seems to be simple and practical. However, if one search the experimental EPR data in the literature will find many examples where the number of spin states (nuclear and electronic) can be very large. This can be the EPR case of an electronic spin $S = 1/2$ surrounded by one ^{63}Cu and four ^{14}N nuclei (as pointed out in Ref. [3]), leading to a situation where the 628 states will result in a generalized eigenvalue problem involving matrices of dimension $628^2 = 394,384$. Depending on the double precision arithmetic of the computing environment, more than 2000 GB of memory will be needed to store one single matrix! Besides, the execution time involved in solving an eigenvalue problem usually scales as the cube of the matrix dimension, what means in the present case, with the six-power of the number of spin states. These are the reasons why the eigenfield approach to the resonance field problem has been restricted to deal with small systems and replaced by approximation methods in the case of large systems.

Since all the restrictions imposed to the eigenfield method are related with Eqs. (8) or (9), we propose here to move backwards, looking more carefully to the Eq. (6) which is defined in the original $n \times n$ state space. We have undertaken a careful search in the literature and we found no published attempts (well succeeded or not) to solve (6) within the $n \times n$ space by means of a numerical procedure. Therefore, we must assume that this is an unpublished subject. We expend some time trying to solve (6) by iterative eigenvalue methods but we concluded that the methodology that will be presented ahead is more conveniently and practical.

Under the light of the FDM we will show that the Eq. (6) can be solved for several real situations. We are still not able to apply our methodology to a broader range of experiments but we consider that there are no fundamental restrictions to do it. For our technical approach to the resonance field problem, we are seeking for a dynamic equation or, more specifically, for a differential equation

for a variable $L(x)$, where x is associated with the magnetic field h . Such equation should have the property that: (i) it has a stationary solution given by Eq. (6) and (ii) the spectral information contained in $L(x)$ should be directly related to the resonance spectrum $I(h)$.

Such intentions may sound unrealistic at first glance, but we are convinced that such equation exists. Instead of investing efforts in first principles calculation one can guess at least two equations that seems to be appropriated to a first analysis. First, we propose here the following first order differential equation:

$$G \frac{d}{dx} L - \left(\frac{d}{dx} L \right) G = 2\pi i [(\Omega I - F)L + LF] \quad (10)$$

It is easy to show that this equation admits solutions like:

$$L(x) = \sum_k M_k e^{i\lambda_k x} \quad (11)$$

The x -independent matrices M_k satisfy the eigenvalue equation:

$$(\Omega I - F)M_k + M_k F = \frac{\lambda_k}{2\pi} (GM_k - M_k G) \quad (12)$$

Comparing this result with Eq. (6) one can notice that both equations are the same if the resonance fields are defined as $h_k = \lambda_k/2\pi$, what means that the variable x has the unit of the reciprocal of the magnetic field.

We have worked with Eq. (10) in a variety of situations and concluded that it is an interesting equation and, if one chooses an appropriate method, it can be solved and its solutions can indeed reproduce all the resonance fields. However, Eq. (10) has pathological characteristics that become evident even in very simple problems. To understand this fact it is convenient to consider the representation where G is diagonal. Then, the Eq. (10) assumes the form:

$$(G_i - G_j) \frac{d}{dx} L_{ij} = 2\pi i \left[\Omega L_{ij} + \sum_k (F_{kj} L_{ik} - F_{ik} L_{kj}) \right] \quad (13)$$

It follows directly that if any eigenvalue of G is degenerated the Eq. (13) will become a system of algebraic-differential equations. Besides, if the degeneracy of G is raised by very small amounts, like what happens when the Zeeman nuclear interaction is included in the EPR Hamiltonian, the possibility of a stiff set of equations arises. Because of these diseases we abandoned this approach looking for a more simple way to achieve our goals.

For a second alternative we choose the following differential equation:

$$(\Omega I - F) \frac{d}{dx} L + \left(\frac{d}{dx} L \right) F = 2\pi i (GL - LG) \quad (14)$$

It is easy to show that this equation admits solutions like (11), where M_k is the solution of the x -independent equation:

$$\frac{\lambda_k}{2\pi} [(\Omega I - F)M_k + M_k F] = GM_k - M_k G \quad (15)$$

Eq. (15) is the same as Eq. (6) if the resonance fields are defined as $h_k = 2\pi/\lambda_k$. We call the attention that, from this result, the variable x has now the unit of magnetic field. If λ_k is named “frequency” the associated resonance field is the corresponding “period”.

The solution matrix, $L(x)$, of Eq. (14) has an important property. By taking into account that the trace of a commutator is null, it is easy to prove that the trace of L is independent of x . Besides, the solution of the equation corresponding to a negative excitation frequency is automatically included when a positive Ω is chosen. This can be understood if Eq. (14) is transposed and conjugated:

$$(-\Omega I - F) \frac{d}{dx} L^H + \left(\frac{d}{dx} L^H \right) F = -2\pi i (GL^H - L^H G) \quad (16)$$

L^H denotes the transpose-conjugate of L . Eq. (16) is identical to Eq. (14) if one exchanges $\Omega \rightarrow -\Omega$ and $G \rightarrow -G$. Replacing G by $-G$ is the same as keeping G unchanged and inverting the magnetic field direction (see Eq. (1)). Therefore, the transpose-conjugate elements of L carry the corresponding solution for a negative excitation frequency coupled to an inversion of the magnetic field direction.

Now, our intention is to solve the differential Eq. (14). As far as we know, such equation has no analytical solution; therefore, we adopted a numerical procedure. We have tried several methods and the forth-order explicit Runge–Kutta method has proved to be convenient for this case. For the initial condition we take a L -matrix were all elements are real and equal to 1 or $L_{ij}(0) = 1$, resulting that the trace of L will be equal to n .

For the case of a first-order Runge–Kutta, known as the Euler method, the Eq. (14) is transformed into an algebraic equation:

$$(\Omega I - F)L_{n+1} + L_{n+1}F = [(\Omega I - F)L_n + L_n F] + 2\pi i (GL_n - L_n G)\Delta x \quad (17)$$

In this expression, $\Delta x = x_{n+1} - x_n$, $L_{n+1} = L(x_{n+1})$, $L_n = L(x_n)$, with the initial condition $L_0 = L(0)$. The extension for the forth-order case is straightforward. Analyzing Eq. (17) we notice that it has the general shape: $PX + XQ = R$, with P , Q and R known matrices and $X = L_{n+1}$, a matrix to be determined. When matrices P and Q are upper triangular, this equation is named “triangular Sylvester equation”, and can be solved by available linear algebra software packages. The matrix F can always be transformed in upper triangular form by Schur factorization, i.e., $F = uTu^H$, where: T is upper triangular, u is unitary and $u^H = u^{-1}$ is the transpose-conjugate of u . Provided that the eigenvalues of P (denoted by α) and those of Q (denoted by β) satisfies: $(\alpha + \beta) \neq 0$ for all α and β , the solution is unique. Therefore, the solution will be always unique—being the only exception the case where the excitation frequency is exactly equal to a zero-field splitting.

The Eq. (14) can be easily solved in the representation in which F is diagonal. In this case it becomes:

$$(\Omega - F_i + F_j) \frac{d}{dx} L_{ij} = 2\pi i \sum_k (G_{ik}L_{kj} - G_{kj}L_{ik}) \quad (18)$$

Provided that $(\Omega - F_i + F_j) \neq 0$ for all i and j , this equation represents a set of ordinary differential equations.

Before we go any further it will be useful to first analyze some examples. From now on, we will consider the EPR case described by the spin Hamiltonian:

$$\mathbf{H} = \mu_B \vec{H} \cdot \vec{g} \cdot \vec{S} - \mu_N g_N \vec{H} \cdot \vec{I} + \vec{S} \cdot \vec{A} \cdot \vec{I} + \vec{S} \cdot \vec{D} \cdot \vec{S} \quad (19)$$

\vec{S} is the electronic spin, \vec{I} is the nuclear spin, μ_B is the Bohr magneton, μ_N is the nuclear magneton, g_N is the nuclear g -factor, \vec{g} is the electronic g -tensor, \vec{A} is the hyperfine coupling tensor and \vec{D} is the zero-field-splitting tensor. The operators \mathbf{F} and \mathbf{G} can be trivially obtained in this case.

2.1. Example 1: the diagonal case

A simple but non-trivial example is the isotropic case $S = 1$ and $I = 1/2$, in which the matrices F and G are diagonal in the basis: $|\alpha_0\rangle = |1, +\rangle$, $|\alpha_1\rangle = |1, -\rangle$, $|\alpha_2\rangle = |0, +\rangle$, $|\alpha_3\rangle = |0, -\rangle$, $|\alpha_4\rangle = |-1, +\rangle$ and $|\alpha_5\rangle = |-1, -\rangle$. The Hamiltonian parameters given by: $g_{zz} = 2.0$, $A_{zz} = 1500$ MHz, $D = 900$ MHz, $E = 0$, $\theta = 0$ and $\varphi = 0$, are assumed. The microwave frequency was set to $\Omega = 9500$ MHz. After building the F and G matrices, the differential Eq. (18) was solved to obtain the x dependency of each element $L_{ij}(x)$.

In Fig. 1 is shown the dependence of L_{52} and L_{04} with x . As predicted by Eq. (11), each one of these functions can be fitted by harmonic functions whose period is the associated resonance field. By drawing the energy level diagram one can verify this affirmation by confirming that at the specified field (or the calculated period) a possible transition can be found. The period (or frequency) associated to different elements of L can be different from each other but the important fact is that all of them can be adjusted to the energy levels splitting and also associated to possible transitions. This is shown in Table 1 where all obtained transitions are assigned to their corresponding L_{ij} . One can notice that all possible transitions can be assigned, except those between hyperfine levels with same m_s whose energy difference is too small for the specified microwave frequency. In this particular example, the diagonal elements of L are independent of x and give no additional information.

The given example is simple but very useful as a guide for the construction of a method capable to find resonance fields in a general situation. If one looks carefully, will see that the elements L_{ij} , which are below the diagonal, give all the information that is necessary to find all the resonance fields of this example. In fact, all the elements above the diagonal are associated to the same transitions that appear in the lower triangle of the matrix, and can be considered as redundant. The element L_{ij} does not correspond to the same transition as that of L_{ji} , therefore, the matrix is not Hermitian. However, for each element above the diagonal there is one below that corresponds to its conjugate, for

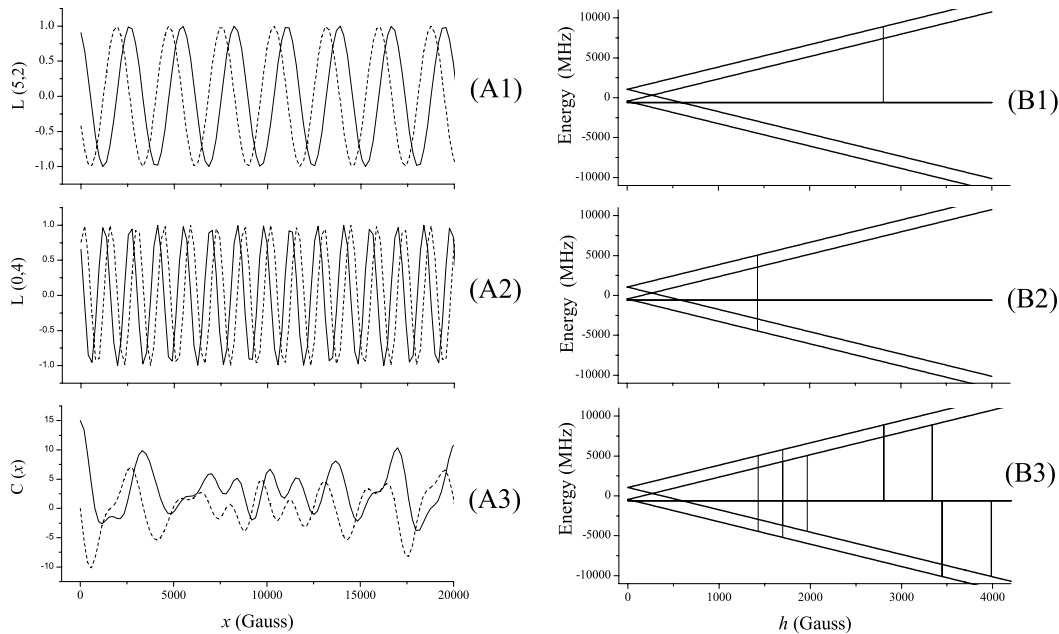


Fig. 1. Matrix elements $L(i,j)$ as a function of magnetic field x (A1, A2) and corresponding energy level transition (B1, B2) for the electronic spin system $S = 1$ and $I = 1/2$ of Example 1. On the left, solid lines correspond to real component and dashed to imaginary. The x -dependence of the sum of the elements of matrix L , $C(x)$ as defined in the text, is shown in (A3) with the corresponding energy level transitions (B3).

Table 1

Map of the matrix L of Example 1 showing the energy level transition corresponding to each matrix element $L_{ij} = L(i,j)$

	0: $ 1,+\rangle$	1: $ 1,-\rangle$	2: $ 0,+\rangle$	3: $ 0,-\rangle$	4: $ -1,+\rangle$	5: $ -1,-\rangle$
0: $\langle 1,+ $			2–5	3–5	0–5	1–5
1: $\langle 1,- $			2–4	3–4	0–4	1–4
2: $\langle 0,+ $	1–3	0–3			0–2	1–2
3: $\langle 0,- $	1–2	0–2			0–3	1–3
4: $\langle -1,+ $	1–4	0–4	3–4	2–4		
5: $\langle -1,- $	1–5	0–5	3–5	2–5		

For example, the element $L(1,3)$ is associated to the transition between levels 3 and 4; the element $L(3,0)$ is associated to the transition between levels 1 and 2. Energy levels are numbered in ascending order of energy. Just for a guide, the basis functions are displayed in the same sequence as used to build the Hamiltonian matrices. Blank elements means absence of associated transitions.

example, $L(0,5) = L(5,0)^*$ and $L(0,4) = L(5,1)^*$. This last fact cannot be generalized, being a simple particularity of this example.

Considering that our interest is to assign all the resonance fields associated to a given spin Hamiltonian we can adopt a procedure in which all elements are analyzed in a single shot, instead of analyze separately each matrix element. This can be accomplished by defining a correlation function:

$$C(x) = \sum_{i=0}^{n-1} \sum_{j<i}^{n-1} L_{ij}(x) \quad (20)$$

The correlation function for the present example is shown in Fig. 1A3. Indeed, these data contain all the information necessary to assign all the resonance fields at once and this can be verified in the energy diagram of

Fig. 1B3. The important question that arises is how this can be done precisely. This question is the most delicate point of our whole discussion and it is related to several aspects of the problem, being the most important one concerned to the spectral resolution. One knows, for example, that hyperfine interactions can lead to line splitting, small as 100 ppm (or even smaller).

2.2. The filter diagonalization method (FDM)

As a starting point, we assume that Eq. (20) is equivalent to a discrete complex signal, c_p , whose analytical form is given by a sum of complex sinusoids:

$$c_p = \sum_{k=0}^{M-1} d_k e^{i p \lambda_k \delta}, \quad p = 0, 1, \dots, N-1 \quad (21)$$

The sampling interval or “dwell time”, δ , and the index $p = 0, 1, 2, \dots, N-1$ define a finite equidistant grid, d_k are the complex amplitudes and λ_k are the frequencies. Here, we will consider that only the cases where λ_k is real have a physical meaning, although, in general, this assumption should not be taken as a necessary condition. We will reconsider this point latter on.

Assuming that the input data size N is large enough, the objective is to find the best “line list”, $\{d_k, \lambda_k\}$, that will fit the data c_p , according to Eq. (21). This problem is known in the literature as the “harmonic inversion problem”, or HIP, and the interesting fact is that it has the property of having a linear algebraic solution, no matter the high non-linearity intrinsic to the HIP. To have the number of unknowns consistent with the number of equations, and to ensure a numerically stable formulation of the HIP, it

is necessary, in principle, to assume $N/2 \geq M$. The method capable to solve this problem is known as the “filter diagonalization method”, or FDM [11,12].

The resolution of the FDM is to be compared with that of the discrete Fourier transform, FT. In the framework of FT, it is well known that the resolution ($1/\Delta\lambda$) in the frequency domain is determined by the uncertainty principle, usually expressed as $\Delta\lambda = 2\pi/(N\delta)$. Hence, the minimum detectable frequency separation between adjacent peaks ($\Delta\lambda$) is inversely proportional to the total acquisition time, $N\delta$. Therefore, the resolution in the resonance field scale ($h = 2\pi/\lambda$) is given by:

$$\Delta h \geq \frac{h^2}{N\delta} \quad (22)$$

In this context, a definition of the doublet centered at 3986 G (see Table 2) with a resolution of 100 ppm would need N to be at least as large as 57,000, assuming that $\delta = 700$ G is the largest measurement interval that satisfies the Nyquist criterion in this case (remembering that the lowest resonance field listed in Table 2 is at about 1400 G). Therefore, the application of the FT in this case would be too expensive.

In the context of FDM, the total number of terms, M , in the sum of Eq. (21), and consequently the number of input data points, N , are irrelevant because the spectral analysis is generally performed locally in the frequency domain. In this case, it is more appropriate to think in terms of the density of information in the frequency domain, i.e. the local density of peaks, $\rho(\lambda)$, should be consistent with the information content of the signal c_p of size N :

$$\frac{N\delta}{4\pi} \geq \rho(\lambda) \quad (23)$$

If this condition is not satisfied, one can only obtain a “low resolution” result in which the “uncertainty” will be due to

the non-unique representation of the time signal in terms of the frequencies λ_k and amplitudes d_k . Otherwise, if the condition is satisfied and the signal c_p of length N has the form of Eq. (21), the FDM will provide “infinite” resolution. In other words, the sampling interval necessary for FDM is proportional to the inverse of the local average line spacing, while for FT the required interval is proportional to the inverse of the local minimum spacing, which can be much longer than the first.

For the case of the plot shown in Fig. 1, were $N = 1024$ and $\delta = 195.5$ G (note that only part of the whole data is shown), the FDM was employed to fit the c_p data and the results obtained for the resonance fields are listed in Table 2. One can observe that the difference between the microwave energy and energy levels separation at each specified resonance field is about 1 ppm, in the worst case, which validates the assumption that the FDM is the appropriate method to solve this problem.

Besides the resolution enhancement, the FDM has several important advantages with respect to FT and other fitting procedures. First of all, one must consider that the maximum number of transitions is given by $(n^2 - n)/2$. However, the number of possible transitions for a given Ω may not be known a priori. In our Example 1, $(n^2 - n)/2 = 15$, but the number of existing transitions is 12. This means that the number of terms in Eq. (21), or M , is unknown, a priori. This fact does not represent a difficulty for the FDM but will impose serious limitations to other common fitting procedures. Another particularity of the FDM is that it ends up with a “line list” with all values of d_k and λ_k that can be available for posterior manipulations. On the contrary, to obtain a line list from the FT spectrum may not be an easy task, because FT is a transformation and not a fitting procedure.

2.3. Example 2: the non-diagonal case

As a second example we will treat an anisotropic case with $S = 2$ and $I = 1$, in which the matrices F and G are not diagonal in the basis $|mS, mI\rangle$, with $mS = 2, 1, 0, -1, -2$ and $mI = 1, 0, -1$. The total number of states is 15, and the Hamiltonian parameters are given by: $g_{xx} = 1.9$, $g_{yy} = 2.1$, $g_{zz} = 2.$, $A_{xx} = 300$ MHz, $A_{yy} = 500$ MHz, $A_{zz} = 1500$ MHz, $D = 1000$ MHz, $E = 400$ MHz, $\theta = 35^\circ$ and $\varphi = 55^\circ$. The microwave frequency was set to $\Omega = 9500$ MHz. After building the F and G matrices, the differential Eq. (18) was solved to obtain the x dependency of $C(x)$ in the range $x = 0$ to $x = 500,000$ G with an increment $\Delta x \approx 6.2$ G. To increase resolution, the FDM was applied twice with two sets of 2048 data points each, extracted from the whole evolution, being the first one with $\delta \approx 290$ G and the second with $\delta \approx 24$ G. Since the lowest and highest resonance fields of this example are, respectively, ≈ 92 and ≈ 4887 G, the first set favors the determination of low frequencies (high field) components while the second improves high frequencies (low field).

Table 2
Resonant fields and corresponding transitions calculated for the Example 1

	Transition	Field-EE (Gauss)	Field-DE (Gauss)	Error (ppm)
1	0–5	1428.9546	1428.9562	0.932
2	0–4	1695.5941	1695.5950	0.559
3	1–5	1698.1751	1698.1760	0.555
4	1–4	1964.8126	1964.8132	0.359
5	2–5	2804.3234	2804.3236	0.0618
6	3–5	2808.5954	2808.5956	0.0614
7	2–4	3335.1086	3335.1087	0.0368
8	3–4	3340.1814	3340.1815	0.0366
9	0–3	3442.1174	3442.1175	0.0335
10	0–2	3447.3530	3447.3531	0.0333
11	1–3	3983.2109	3983.2110	0.0216
12	1–2	3989.2787	3989.2788	0.0215

Resonant fields calculated from the eigenvalue equation (Eq. (8)) are denoted by Field-EE and those calculated from the differential equation (Eq. (18)) by Field-DE. The FDM was used to fit the $C(x)$ data to Eq. (21). The indicated errors correspond to the deviation, in ppm, between the microwave energy and levels separation at each specified resonance field calculated from Eq. (18).

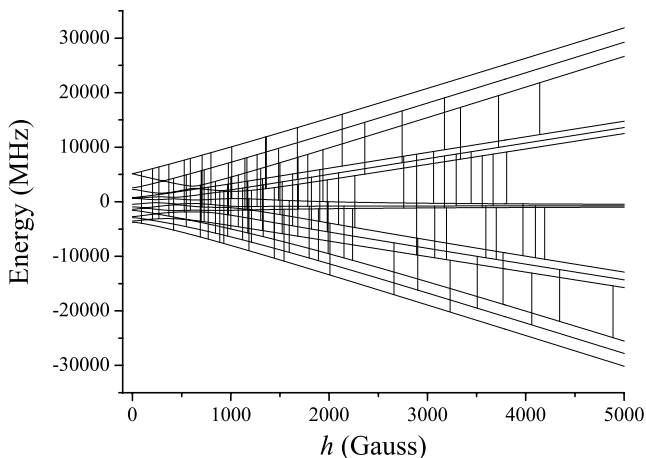


Fig. 2. Energy level transitions diagram for the electronic spin system $S = 2$ and $I = 1$ of Example 2.

The results of this theoretical example are shown in Fig. 2. The x dependency of $C(x)$ is very messy and is not shown but its decomposition by FDM recovers almost exactly all the 90 resonance fields allowed for this case. The error between the microwave energy and energy levels separation at each specified resonance field is in the worst case less than 10 ppm.

2.4. Example 3: the singular case

When the microwave frequency is exactly equal to a zero field splitting one or more coefficients, $(\Omega - F_i + F_j)$, on the left side of Eq. (18) will be null, then the equation will represent a system of algebraic-differential equations, which cannot be solved by the simple procedure that we have adopted before. Instead of using more complicated methods capable to solve such kind of equations, we adopted here a more simple procedure, which is based on a valid trick that consists in modulate the microwave frequency.

For the first Runge–Kutta step we take a microwave frequency, Ω_1 , that is slightly above the desired frequency, Ω , such that $\Omega_1 = \Omega + \Delta_1$. For $\Omega \approx 9500$ MHz, a good choice can be Δ_1 in the range 50–100 MHz. For the second step, the frequency is changed to $\Omega_2 = \Omega - \Delta_2$ and the value of Δ_2 is calculated for each one of the equations of the set (18) according to the prescription:

$$\frac{1}{\Omega_1 - F_i + F_j} + \frac{1}{\Omega_2 - F_i + F_j} = \frac{2}{\Omega - F_i + F_j}, \text{ if } \Omega - F_i + F_j \neq 0$$

$$\Omega_1 = \Omega + \Delta_1 \text{ and } \Omega_2 = \Omega - \Delta_1, \text{ if } \Omega - F_i + F_j = 0$$

(24)

Then, the same procedure is repeated for all steps, i.e., applying Ω_1 for odd steps and Ω_2 for even steps. The result of this manipulation is excellent; the method works well in the case where $(\Omega - F_i + F_j) = 0$ for some components (i, j) and also when $(\Omega - F_i + F_j)$ is not null for all components.

To demonstrate the utility of this method we will continue to use the Example 1, slightly modified by changing

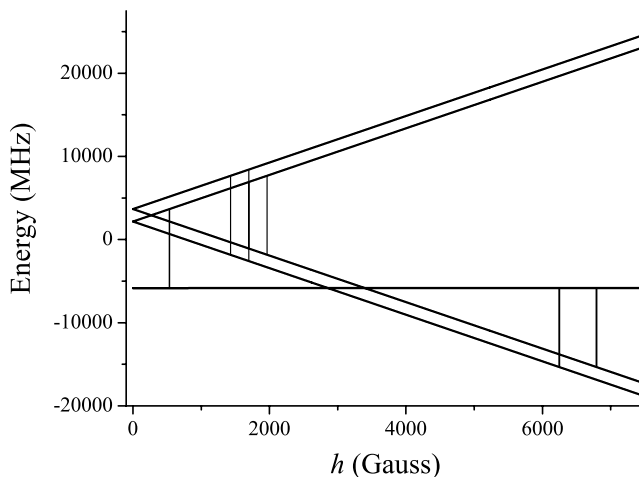


Fig. 3. Energy level transitions diagram for the electronic spin system $S = 1$ and $I = 1/2$ of Example 3. The zero-field transition is not shown.

the value of the zero-field-splitting parameter to $D = 8750$ MHz. For this situation there will be a zero-field transition. The solution of Eq. (18), taking $\Delta_1 = 100$ MHz, is stable and the application of the FDM to the correlation function $C(x)$ gives the resonance fields shown in Fig. 3. The 10 transitions that exist for $h > 0$ were correctly calculated and the difference between the microwave energy and energy levels separation at each specified resonance field is again of the order of few ppm, in the worst case. Of course, the transitions that exist for $h = 0$ cannot be calculated from this method but they can be easily determined a priori.

To be fair, we must explain that the above method worked well for the chosen example but it cannot solve all experimental situations in general. The reason why it could solve this example can be understood in the following way. If one uses the eigenvalue equation, Eqs. (8) or (9), to find the resonance fields of this particular example will encounter that all the eigenvalues are real in the two situations: $\Omega = \Omega_1$ and $\Omega = \Omega_2$. This is not a general result because, in general, complex eigenvalues will be found when $(\Omega - F_i + F_j)$ is negative for some pairs (i, j) . As will be discussed below, complex eigenvalues represent a problem that we cannot solve yet.

2.5. Limitations of the proposed method

Here, we will discuss about one serious limitation of the methodology here proposed with the objective to determine all the resonance fields of any physical system described by the Hamiltonian of Eq. (19).

In our early discussion concerning the generalized eigenvalue Eq. (8), we emphasized that if the matrix A is not positive-definite some of the eigenvalues may result complex. This is the situation where $(\Omega - F_i + F_j)$ is negative for some pairs (i, j) . Although the procedure we are proposing is different from the eigenvalue method, one can observe that the

Eq. (18), used throughout this work, will become equivalent to Eq. (8) if the matrix L is written as a column vector. Therefore, the same restrictions that were mentioned with respect to the eigenvalue method also apply here.

When some of the eigenvalues are complex, the general solution for $L(x)$, given by Eq. (11), will represent complex sinusoids with amplitudes that may decay or grow as x increases. The differential Eq. (18) can still be solved in this situation, since the problem still remains well conditioned. Also, after $C(x)$ being correctly calculated there will be no problem in applying the FDM, because it is a tool specially designed to deal with such more general situation. Therefore, in principle, when $(\Omega - F_i + F_j)$ is negative the correlation function $C(x)$ can still be determined and the FDM should be capable to find all the resonance fields, including the complex ones.

The problem that arises when $(\Omega - F_i + F_j)$ is negative is purely technical. The fact is that the exponentially growing functions, of the type $e^{\gamma x}$ with γ positive, have a characteristic time rate, γ , of the same order of magnitude of the corresponding frequency of the harmonic functions that they modulate. This means that after few Runge–Kutta steps these complex eigenvalues will dominate the evolution of $L(x)$ and every element $L_{ij}(x)$ will grow so rapidly in amplitude that the accuracy needed to determine the weak features represented by pure harmonic functions is degraded.

We have tried many alternative methods to solve the Eq. (18) under these circumstances but we could not reach a final conclusion. It is apparent that the inclusion of an appropriate damping term could be able to control the growing rate of the undesired solutions without spoiling the desired ones. However, we are still working on this subject.

3. Conclusions

The new method described herein has the objective to determine the resonance fields of a given spin Hamiltonian. Its formulation is based on one hypothesis, i.e., that the Eq. (14) is valid. Then, the method is capable to calculate precisely, in a single shot, all the resonance fields without the need to solve eigenvalue equations or sophisticated algorithms. We have shown here just few examples, but we have worked on many other examples, chosen for testing purposes, which are not shown in here. In all cases the method was able to determine all the resonance fields with a precision of the order of few ppm.

Because of a technical reason, the method cannot be applied when the microwave energy does not cover the overall zero-field splitting but, at least for the remaining cases, it has the potential to become a routine method since it is stable, robust and does not require more user effort than other methods. Since we were more concerned to the precision of

the method, we have not applied sufficient efforts to optimize our software routines, so far. Therefore, we have no means to compare the efficiency of our method with that of other available software packages that were built for the same purposes.

We expect that this new tool will enhance the versatility of the EPR spectra simulation methods.

Acknowledgments

The authors really appreciated the many fruitful discussions and helpful suggestions of our colleague Prof. Jayme Vicente de Luca Filho. This work was supported by the Brazilian agencies Conselho Nacional de Desenvolvimento Científico, CNPQ, Fundação de Amparo à Pesquisa do Estado de São Paulo, FAPESP, and is part of a joint program PRONEX/FAPESP/CNPq (Grant No. 03/09859-2).

References

- [1] R.L. Belford, M.J. Nilges, Computer simulation of powder spectra, EPR Symposium, 21st Rock Mountain Conference, Denver, Colorado (August, 1979).
- [2] Nilges, M.J. (1979) Electron Paramagnetic Resonance Studies of Low Symmetry Nickel (I) and Molybdenum (V) Complexes. Ph.D. thesis, University of Illinois, Urbana, IL.
- [3] S. Stoll, A. Schweiger, EasySpin, a comprehensive software package for spectral simulation and analysis in EPR, *J. Magn. Reson.* 178 (2006) 42–55.
- [4] G.G. Belford, R.L. Belford, J.F. Burkhalter, Eigenfields: a practical direct calculation of resonance fields and intensities for field-swept fixed-frequency spectrometers, *J. Magn. Reson.* 11 (1973) 251–265.
- [5] M.I. Scullane, L.K. White, N.D. Chasteen, An efficient approach to computer simulation of EPR spectra of high-spin Fe(III) in rhombic ligand fields, *J. Magn. Reson.* 47 (1982) 383–397.
- [6] P.C. Taylor, J.F. Baugher, H.M. Kritz, Magnetic resonance spectra in polycrystalline solids, *Chem. Rev.* 75 (1975) 203–240.
- [7] M. Griffin, A. Muys, C. Noble, D. Wang, C. Eldershaw, K.E. Gates, K. Burrage, G.R. Hanson, Xsophe, a computer simulation software suite for the analysis of electron paramagnetic resonance spectra, *Mol. Phys. Rep.* 26 (1999) 60–84.
- [8] D. Nettar, J.J. Villafranca, A program for EPR Powder spectrum simulation, *J. Magn. Reson.* 64 (1985) 61–65.
- [9] S.K. Misra, Evaluation of Spin-Hamiltonian parameters from EPR data by the method of least-squares fitting, *J. Magn. Reson.* 23 (1976) 403–410.
- [10] K.E. Gates, M. Griffin, G.H. Hanson, K. Burrage, Computer simulation of magnetic resonance spectra employing homotopy, *J. Magn. Reson.* 135 (1998) 103–112.
- [11] V.A. Mandelshtam, H.S. Taylor, Harmonic inversion of time signals and its applications, *J. Chem. Phys.* 107 (1997) 6756–6769.
- [12] V.A. Mandelshtam, FDM: the filter diagonalization method for data processing in NMR experiments, *Prog. Nucl. Magn. Reson. Spectrosc.* 38 (2001) 159–196.
- [13] J.H. Wilkinson, *The Algebraic Eigenvalue Problem*, Clarendon Press, Oxford, 1965.