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### A new Lanczos-based algorithm for simulating high-frequency two-dimensional electron spin resonance spectra

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The Lanczos algorithm (LA) is a useful iterative method for the reduction of a large matrix to tridiagonal form. It is a storage efficient procedure requiring only the preceding two Lanczos vectors to compute the next. The quasi-minimal residual (QMR) method is a powerful method for the solution of linear equation systems, Ax = b. In this report we provide another application of the QMR method: we incorporate QMR into the LA to monitor the convergence of the Lanczos projections in the reduction of large sparse matrices. We demonstrate that the combined approach of the LA and QMR can be utilized efficiently for the orthogonal transformation of large, but sparse, complex, symmetric matrices, such as are encountered in the simulation of slow-motional 1D- and 2D-electron spin resonance (ESR) spectra. Especially in the 2D-ESR simulations, it is essential that we store all of the Lanczos vectors obtained in the course of the LA recursions and maintain their orthogonality. In the LA-QMR application, the QMR weight matrix mitigates the problem that the Lanczos vectors lose orthogonality after many LA projections. This enables substantially more Lanczos projections, as required to achieve convergence for the more challenging ESR simulations. It, therefore, provides better accuracy for the eigenvectors and the eigenvalues of the large sparse matrices originating in 2D-ESR simulations than does the previously employed method, which is a combined approach of the LA and the conjugate-gradient (CG) methods, as evidenced by the quality and convergence of the 2D-ESR simulations. Our results show that very slow-motional 2D-ESR spectra at W-band (95 GHz) can be reliably simulated using the LA-QMR method, whereas the LA-CG consistently fails. The improvements due to the LA-QMR are of critical importance in enabling the simulation of high-frequency 2D-ESR spectra, which are characterized by their very high resolution to molecular orientation. © 2011 American Institute of Physics. [doi:10.1063/1.3523576]

#### I. INTRODUCTION

Spin-label electron spin resonance (ESR) spectroscopy has, in recent years, been widely used and demonstrated as a powerful tool to investigate the local dynamics and structure of complex fluids such as liquid crystals and model and biological membranes, polymers, proteins, and protein complexes.<sup>1–4</sup> Among the various ESR techniques, continuous-wave (cw) ESR has been successfully extended to high magnetic fields.<sup>2–6</sup> The greatly improved orientational resolution that is provided by the ESR lineshapes in high frequencies/fields provides a better insight to the molecular dynamics.<sup>2–5</sup> By means of multi-frequency ESR experiments, one can unravel the details of dynamical modes of the complex systems since the different frequencies provide different time windows.<sup>2–5,7</sup>

In recent years, it has been shown that 2D-ESR methods, in particular 2D-ELDOR (electron-electron double resonance) studies on complex fluids and macromolecules provide even greater spectral resolution to molecular dynamics and ordering.<sup>2,3,8</sup> 2D-ELDOR provides this, because it enables one to distinguish the homogeneous broadening (which provides insight into molecular motions) from the inhomogeneous broadening (which relates to local structure). Furthermore, it supplies cross-peaks that directly report on translational and rotational motions of labeled biomolecules. Recent technological developments have led to the capability of performing 2D-ELDOR on complex fluids at high frequency (95 GHz), which can then combine their respective virtues.<sup>5,9</sup>

The theoretical prediction and interpretation of these ESR spectra requires a special analysis developed by Freed and coworkers based on the stochastic Liouville equation (SLE).<sup>10</sup> This approach has been effectively extended to 2D-ELDOR,<sup>11</sup> and it has been successfully applied to such experiments performed at conventional ESR frequencies (9 and 17 GHz).<sup>3,8</sup> However, we found that the existing methods are not versatile enough to permit the successful computation of high-frequency 2D-ESR spectra in the (very) slow motional regime because of serious convergence issues that are significantly more demanding than at conventional frequencies. In the present paper, we report on recent progress we have made in improving the computational algorithms to enable the simulation of high-frequency 2D-ESR spectra over the whole motional range.

The primary challenge is to reliably diagonalize the very large matrix representation of the SLE operator, which

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becomes extremely large for high-frequency spectra. It was shown some time ago that the Lanczos algorithm (LA) as applied to large and sparse but complex symmetric matrices, is a most effective algorithm for reducing the SLE and related correlation function matrix representations to tridiagonal form.<sup>10–15</sup> It was also shown that the resultant eigenvalues (and eigenvectors) are approximations to the exact ones, but nevertheless yield accurate spectra.<sup>10,13</sup> The LA<sup>16</sup> is now a well-known and very effective method for reducing a large matrix to tridiagonal form. It has also been extensively used in other applications in chemical physics.<sup>17</sup> It is an iterative subspace method that operates by generating a set of basis vectors, induced by the SLE operator, A, producing what is known as the Krylov subspace wherein A is tridiagonal, and can readily be diagonalized. The dimension  $(n \times n)$  of the original matrix **A** is much larger than the dimension  $(m \times m)$  of the reduced tridiagonal matrix (i.e., the Krylov subspace) that is needed to represent the physical observable (e.g., the ESR spectrum). However, the Lanczos projections must be carefully monitored to determine when a convergent Krylov subspace has been achieved. A special approach, combining the LA method of tri-diagonalization with the method of conjugate gradients was developed specifically for this purpose.<sup>10,15</sup> This overall procedure for tridiagonalization is called the LA-CG algorithm in the present report; this is to be distinguished from CG-type algorithms, which are used as linear equation solvers.

On the one hand, when the LA-CG is utilized for constructing the Krylov subspaces, the primary issue is how well the (relevant) eigenvalues, and eigenvectors generated from this subspace are representative of the original matrix. On the other hand, when the LA combined with CG is used for solving a linear equation system, Ax = b (or equivalently  $A|x\rangle$ )  $= |b\rangle$ ), one does not solve for the eigenpairs, but focuses on the convergence of the residual norm of the linear equation to obtain a good enough approximation for the solution vector  $|x\rangle$  instead.<sup>18</sup> The former application (i.e., our present interest) often requires a much larger number of the Lanczos projections than does the latter. The main reason is that as the Lanczos steps proceed, the eigenvalues calculated from the Krylov subspace that is generated, consist of good ones, duplicates, and spurious ones. Identifying good eigenvalues and determining how many Lanczos projections are enough to obtain a reduced matrix that has sufficiently converged to produce the required set of good eigenvalues, is itself a difficult task. It is this computational challenge that becomes even greater as one performs the spectral simulation of higher frequency ESR experiments. Therefore, one often finds that the use of the LA-CG becomes extremely troublesome, given that physically important eigenvalues appear late in the LA procedure, thereby demanding a large number of LA projections. This is a key reason why the number of LA projections increases significantly as the molecular motional rates become slower and the original  $N \times N$  matrix representation of A becomes larger.

In the present report, we demonstrate that increasing the number of LA projections (i.e., increasing the dimension m of the Krylov subspace) is not necessarily a guarantee of the success of the LA-CG in calculating the slow-motional line-

shapes. This situation (that we call the LA-CG breakdown) becomes even worse as the ESR frequency increases. To deal more effectively with the breakdown, we utilize the quasiminimal residuals (QMR) method to replace CG in the Lanczos procedure.

It is important to point out that the computation of timedomain 2D-ESR experiments poses a greater challenge than does that for the 1D experiments (either cw or equivalently free-induction decays). This is because the latter requires just the projection of the reduced  $m \times m$  matrix on a "starting vector" representing the nature of the physical observable in the form of a generalized transition moment, and this effectively, and automatically, discards unwanted eigenpairs.<sup>10, 12, 14</sup> In fact, only the projection of each eigenvector on the "starting vector" is needed, not the full eigenvector.<sup>10,12,14</sup> In the case of 2D-ESR experiments, one requires an accurate set of eigenvectors as well, to properly represent the (complex) orthogonal transformations that are needed in multi-pulse sequences.<sup>10</sup> This requirement is discussed in considerable detail by Lee et al.,<sup>11</sup> who show the limitations (i.e., range of validity) of the LA-CG method in 2D-ESR. They do employ a method of Cullum and Willoughby<sup>16</sup> for identifying spurious eigenvalues, which enabled them to extend this range of validity somewhat.

The QMR algorithm was originally developed for the iterative solution of large non-Hermitian linear systems.<sup>19,20</sup> It is generally used along with the LA to solve a linear equation system, in the same spirit as the CG-based method for the iterative solution of linear systems,<sup>20,21</sup> that we have mentioned above. It was shown that the QMR-based method for the solution of large sparse linear systems with complex coefficient matrices outperforms the CG-based method with several advantages, such as faster convergence.<sup>18</sup> However, the QMR algorithm has not previously (to our knowledge) been used to monitor the LA projection steps for the purpose of generating the orthogonal transformation needed to tridiagonalize sparse matrices, which is the application we address in the present report.

In Section II we review the basic lineshape theory required to simulate 2D-ESR spectra, followed by the computational formulation required to solve for the eigenmodes of the stochastic Liouville operator. We then discuss breakdowns that may occur with the LA-CG as it is used to simulate high-frequency 2D-ELDOR spectra in the slowmotional regime. The new Lanczos-based algorithm, i.e., the combined approach of the LA and the QMR algorithms, is then presented. Some numerical experiments are presented in Section III to illustrate these matters. A brief summary and conclusions are given in Section IV.

#### **II. THEORY AND COMPUTATIONAL ALGORITHMS**

## A. Simulation of 2D-ELDOR spectra using the stochastic Liouville equation

The dynamics of spin-bearing molecules can be treated quantum mechanically and characterized by the modified density matrix  $\chi(\Omega, t) \equiv \rho(\Omega, t) - \rho_{eq}(\Omega)$  satisfying the



FIG. 1. The matrix computational flowchart of solving for the diagonal transformation of the stochastic Liouville operator matrices A.

stochastic Liouville equation<sup>11,12</sup>

$$\frac{\partial}{\partial t}\chi(\Omega,t) = -[iH^{\times}(\Omega) + \Gamma(\Omega)]\chi(\Omega,t)$$
  
$$\equiv -L(\Omega)\chi(\Omega,t)$$
(1)

where  $H^{\times}(\Omega)$  is the commutator superoperator of the spin Hamiltonian, which depends on the orientation of the molecule as specified by its Euler angles  $\Omega$ .  $\Gamma(\Omega)$  is the timeindependent Markovian operator representing the molecular motion. Their sum constitutes the stochastic Liouville operator  $L(\Omega)$ . Also  $\rho(\Omega, t)$  is the density matrix evolving according to  $L(\Omega)$  and  $\rho_{eq}(\Omega)$  is its form at equilibrium. The matrix representation of  $L(\Omega)$  is denoted by **A** throughout this paper. The formal solution to Eq. (1) can be written as

$$\chi(\Omega, t + t_0) = \exp\left(-L(\Omega)t\right)\chi(\Omega, t_0).$$
<sup>(2)</sup>

Equation (2) clearly shows that the evolution of the density matrix is fully characterized by the eigenmodes of the stochastic Liouville operator (or, equivalently, the matrix A). The main task of simulating ESR lineshapes can be regarded, in terms of matrix computations, as the diagonalization of A.

The details for the evolution of the density matrix, including the effect of several pulses, can be found in Lee *et al.*<sup>11</sup> The expressions for the 2-pulse 2D-COSY and the 3-pulse 2D-ELDOR experiments<sup>11</sup> are given in bra-ket notation in Eqs. (3)

$$S_{c\pm}^{COSY} = \langle v_{-1} | O_{-1}e - \Lambda_{-1}t_2 O_{-1}^{tr} \\ \times P_{(-1 \leftarrow \mp 1)} O_{\mp 1}e^{-\Lambda_{\mp 1}t_1} O_{\mp 1}^{tr} | v_{\mp 1} \rangle$$
(3a)

$$S_{c\pm}^{ELDOR} = \langle v_{-1} | O_{-1}e - \Lambda_{-1}t_2 O_{-1}^{tr} P_{(-1 \leftarrow 0)} O_0 e^{-\Lambda_0 T_m} O_0^{tr}$$

$$\times P_{(0\leftarrow\mp1)}O_{\mp1}e^{-\Lambda_{\mp1}t_1}O_{\mp1}^{tr}|\upsilon_{\mp1}\rangle \tag{3b}$$

where  $P(_{b\leftarrow a})$  represent the pulse propagators that transform the density matrix elements from *a* subspace to *b* subspace, as a result of nonselective  $\pi/2$  pulses (where subscripts *a* and *b* give the electron-spin coherence order).  $|\upsilon\rangle$  represents the starting column vector, which is constructed from the spin transition moment averaged over the equilibrium distribution in  $\Omega$ ;  $O_a$  is the orthogonal transformation matrix, whose columns represent the eigenvectors of **A**, and  $\Lambda_a$  is the diagonal matrix of the corresponding eigenvalues, with subscript *a* again referring to the coherence order for the sub-space. The sub-matrices of **A** (i.e., **A**<sub>a</sub>) corresponding to the different coherences are diagonalized via the respective orthogonal transformation. The values of a = 0 correspond to the diagonal and  $a = \pm 1$  the off-diagonal subspaces, respectively.

A complete analysis of the solution of Eqs. (3) was presented in Lee et al.<sup>11</sup> We provide a brief summary below, focusing on the key computational aspects of the SLEbased spectral simulations that are directly relevant to the issues addressed in this paper. The main computational challenge involves first the reduction to the relevant  $m_a \times m_a$  subspaces and then the diagonalization of the SLE submatrices  $A_a$ , for each coherence order which can be extremely large, but are sparse, complex symmetric (and thus non-Hermitian). The approach that has been effectively utilized involves a three-step procedure, which is summarized in the diagram of Fig. 1. First of all, we perform  $m_a$  steps of Lanczos projection on the  $N_a \times N_a$  matrix  $A_a$  to obtain the tridiagonal matrix,  $\mathbf{T}_a$  of dimension  $m_a \times m_a$ . One requires that  $m_a$  is determined by the convergence criteria in the Lanczos-based algorithm and is (much) smaller than  $N_a$ . The transformation matrix,  $V_a$  is also needed, since it is used to determine the eigenvectors (or eigenmodes) which are needed according to Eqs. (3) to provide the 2D-ESR spectra. That is,  $V_a$  represents the set of Lanczos column vectors that tridiagonalize the original sparse matrix  $A_a$ . The QL algorithm<sup>23</sup> is usually used to calculate the  $m_a$  eigenvalues of the tridiagonal matrix  $T_a$ , by a series of orthogonal transformations to obtain the diagonal matrix  $\Lambda_a$ . It is common for the eigenvalues obtained in the Lanczos process that the  $m_a$  eigenvalues consist of "good," "duplicate," and "spurious ones," where the latter are less accurate or "ghost" eigenvalues. The sorting of spurious eigenvalues from the good eigenvalues is nontrivial, since the number of these extra eigenvalues and their location in

the spectrum varies with  $m_a$ , i.e., with the number of Lanczos projections. An identification test may be performed using the Cullum–Willoughby method<sup>16–23</sup> which we have employed in this work.

In the above we have a = 0 or  $\pm$ . However, there is an important distinction between the particular starting vectors used for the off-diagonal subspaces  $(a = \pm 1)$  and the diagonal subspace (a = 0). We consider the former first and the latter below. The starting vector for  $a = \pm 1$  is the ket  $|v_{\pm}\rangle$  shown in Eqs. (3) and the tridiagonal matrices  $\mathbf{T}_{\pm}$  are generated by successive applications of  $\mathbf{A}_{\pm}$  using  $|v_{\pm}\rangle$ . These projections are essentially those used to generate the cw spectrum.

This observation has led us in the present work to add a further filtering procedure to discard the eigenvalues of large magnitude that are considered of less significance in the 2D spectra. The contribution of the eigenvectors contained in the cw-ESR lineshapes is estimated according to the weight factors, calculated in the QL<sup>23</sup> procedure, in the analysis of the continued fraction expansion.<sup>22</sup> The underlying idea behind this is that the cw calculation generates continued fractions that tend to optimize the overall shape of the spectrum rather than sets of eigenvalues. After the identification procedure, a size of  $m'_{\pm}$  of the diagonal eigenvalue matrix, where m'< m, is obtained and ready to be used for simulating 2D-ESR time-domain signals using Eqs. (3). The set of the eigenvectors  $\mathbf{Q}'_{\pm}$ , which correspond to the  $m'_{\pm}$  selective eigenvalues, is calculated using the Inverse Iteration method.<sup>16</sup> The orthogonal transformation matrix  $\mathbf{O}_{\mp}$ , which diagonalizes the original sparse matrix  $A_{\mp}$ , is then obtained in this so-called back-transformation procedure, i.e.,  $\mathbf{O}_{\pm} = \mathbf{V}_{\pm} \mathbf{Q}'_{\pm}$ , using the iterated Lanczos vectors  $V_{\pm}$  and the eigenvectors  $(Q'_{\pm})$  of  $\mathbf{T}_{\pm}$ . It, therefore, is essential to store all of the eigenvectors (both  $V_{\pm}$  and  $Q'_{\pm}$ ) in simulating the 2D ESR spectrum. The overall procedure in Fig. 1 summarizes the orthogonal transformation of a large, sparse, symmetric, and non-Hermitian matrix by a Lanczos-based algorithm. It has been proved to lead to a significant reduction in computation time, which is the key aspect that makes the nonlinear least-squares fitting of the SLE-based lineshape theory to experimental data practically applicable and efficiently executable.

We note the construction of the matrix  $A_a$  that represents the stochastic Liouville operator in the following. ESR spectra can be calculated to a good approximation by finite matrices  $A_a$ , which have large enough leading dimension  $N_a$ . However, one wishes to truncate the space so as to minimize  $N_a$  to be just enough for the accurate computation of the spectra. This is accomplished using the minimum truncation scheme (MTS), developed by Vasavada *et al.*,<sup>15</sup> for representing  $|v_{\pm 1}\rangle$ and  $A_{\pm}$  in order to (1) avoid having to implement too many Lanczos recursions that would possibly cause breakdowns (see below), (2) yet guarantee that the results have converged, and (3) minimize the computation time. Our approach is to start with a basis set large enough to contain the MTS. The dimension of  $A_{\pm}$  can then be reduced after first determining the range of values of the dynamical parameters needed to fit the experimental spectra. Determining the MTS is time consuming, but worthwhile, since it saves a large amount of computation time in the non-linear least-squares fitting to experiment. Tables, derived from empirical rules, for selecting MTS for different regimes of molecular rotational motions can be found in the literature.<sup>22</sup>

For the diagonal sub-space (a = 0), it is necessary to construct an appropriate starting vector. Lee *et al.*<sup>11</sup> have introduced the following procedure based on Eq. (3b). One first calculates

$$|c(t_{1})\rangle \equiv P_{(0 \leftarrow \mp 1)} O_{\mp 1} e^{-\Lambda_{\mp 1} t_{1}} O_{\mp 1}^{tr} |\upsilon_{\mp 1}\rangle$$
(4)

for several values of  $t_1$ . A superposition of these  $|c_0(t_1)\rangle$  is taken as a relevant starting vector for the LA using  $\mathbf{A}_0$ . One benefits from first using the MTS for  $|v_{\pm 1}\rangle$  as well as the  $\mathbf{O}_{\pm} = \mathbf{V}_{\pm} \mathbf{Q}'_{\pm}$  matrices, which have been filtered as described above.

### B. Lanczos-based methods for the orthogonal transformation: LA-CG versus LA-QMR

From the previous section, the important issue that remains to be addressed is how to determine the number of the Lanczos projections required to obtain the dominant eigenvalues of the SLE matrix for the given values of the motional parameters. The orthogonal transformation for diagonalizing the matrix **A** can be performed using the Lanczosbased algorithms, including (1) Lanczos-Conjugate-gradient (LA-CG), which has been used extensively in ESR lineshape simulations, and (2) the Lanczos-Quasi-minimal-residual (LA-QMR), which is to be introduced below. Though the underlying principles of the two methods for reduction transformation are similar, we, in the following, first review the LA-CG in order to clearly display the improvements that we can make with the use of LA-QMR.

We first note that the breakdown in the LA-CG procedure that we are about to discuss below is different from a wellknown LA breakdown. This well-known LA breakdown<sup>24</sup> occurs in the standard nonsymmetric Lanczos process when a quasinull space occurs, i.e., division by zero in the Lanczos projections, before an invariant subspace is found. In finite precision arithmetic, such exact breakdowns are very unlikely; whereas, near-breakdowns may occur and lead to numerical instabilities in subsequent Lanczos projections. The look-ahead version<sup>25</sup> of Lanczos algorithm is dedicated to curing this breakdown for nonsymmetric matrices. The symmetric Lanczos process for Hermitian matrices is a special case of the general procedure where the occurrence of the breakdown can be excluded.<sup>18</sup> In all of our numerical experiments performed in this and previous studies, such a breakdown caused by approaching quasinull subspace has never happened.

#### 1. LA-CG algorithm

The standard single-vector Lanczos recursion is shown in Eq. (5). The iteration of Eq. (5) results in a reduced symmetric tridiagonal matrix whose diagonal and off-diagonal elements are shown in Eqs. (6a) and (6b), respectively. In exact arithmetic the Lanczos projections stop when  $\beta_{k+1} = 0$ ; whereas, in genuine applications such a condition never happens. The Lanczos recursion can be written in a compact matrix form shown in Eq. (7), where **A** is the matrix to be tridiagonal-

ized,  $V_k$  (called the Lanczos vector set) is a matrix consisting of *k* Lanczos column vectors, and  $T_k$ , explicitly shown in Eqs. (7), (7b) and (7c), represents the tridiagonal matrix at the *k*th Lanczos projection. The Lanczos procedure builds up  $V_k$ by one column per recursion,

$$\beta_{k+1} |\nu_{k+1}\rangle = A |\nu_k\rangle - \alpha_k |\nu_k\rangle - \beta_k |\nu_{k-1}\rangle.$$
(5)

$$\alpha_k \equiv \langle \nu_k \, | A | \, \nu_k \rangle \tag{6a}$$

$$\beta_{k+1} \equiv \langle v_{k+1} | A | v_k \rangle \,. \tag{6b}$$

$$AV_k = V_{k+1}\tilde{T}_k \tag{7}$$

$$\tilde{T}_k := \begin{bmatrix} T_k \\ \beta_{k+1} e_k^{tr} \end{bmatrix} \text{ with } e_k^{tr} := [0 \cdots 0 \ 1]$$
(7b)

$$T_{k} = \begin{bmatrix} \alpha_{1} & \beta_{2} & 0 & \dots & 0 \\ \beta_{2} & \alpha_{2} & \beta_{3} & \ddots & 0 \\ 0 & \beta_{3} & \alpha_{3} & \ddots & 0 \\ \vdots & \ddots & \ddots & \ddots & \beta_{k} \\ 0 & \dots & 0 & \beta_{k} & \alpha_{k} \end{bmatrix}.$$
 (7c)

Note that with A complex symmetric, the Lanczos vectors  $|v_k\rangle$  are normalized with a complex orthogonal norm, with the  $|\nu_k\rangle$  referred to as rectanormal vectors.<sup>10</sup> In order to monitor the recursions, the LA is incorporated into the CG procedure to become an equation solver for a linear equation such as  $\mathbf{A}|x\rangle = |b\rangle$ .<sup>14</sup> In each step of the Lanczos recursion, the convergence is monitored according to the residual norm [shown in Eq. (8)], calculated in the CG iterations, since Eq. (8b) represents a measure of the deviation of the column vector  $|x_k\rangle$  from the true solution. Equation (8) clearly shows that the residual values are calculated directly using the quantities obtained in the Lanczos recursions as well as the CG iterations. Note that the LA is started from k = 0 with  $|r_1\rangle = |b\rangle$ , which implies the initial solution vector is zero  $(|x_1\rangle = 0)$ , in order to obtain the correspondence between the Lanczos vectors and the residual vectors,

$$\begin{aligned} |\langle r_k | r_k \rangle \| &= ((\beta_1 | e_1 \rangle - \tilde{T}_k | y_k \rangle)^{tr} V_{k+1}^{''} V_{k+1}(\beta_1 | e_1 \rangle \\ &- \tilde{T}_k | y_k \rangle))^{1/2} \equiv \rho_k, \end{aligned}$$
(8)

$$|r_{k}\rangle = |b\rangle - A |x_{k}\rangle = |r_{1}\rangle - V_{k+1}\tilde{T}_{k} V_{k}^{tr} |x_{k}\rangle$$
  
$$= V_{k+1} \left(\beta_{1} |e_{1}\rangle - \tilde{T}_{k} V_{k}^{tr} |x_{k}\rangle\right). \quad (8b)$$
  
$$= V_{k+1} \left(\beta_{1} |e_{1}\rangle - \tilde{T}_{k} |y_{k}\rangle\right)$$

where  $|\beta_1\rangle = \langle r_1 | r_1 \rangle^{1/2}$  and  $|y_k\rangle \equiv V_k^{tr} | x_k \rangle$ . Freed and co-workers<sup>10</sup> demonstrated clearly that the elements of the tridiagonal matrix can be equivalently obtained by directly using the quantities at each CG step, as shown below [Eqs. (9a) and (9b)] where  $|p_k\rangle$  represents a set of conjugate directions given at the *kth* CG iteration and  $\rho$ 's [cf. Eq. (8)] are the residual norms of the CG iterations,

$$\alpha_{k} = \rho_{K}^{-2} \langle p_{k} | A | p_{k} \rangle + \left( \rho_{k}^{2} \rho_{k-1}^{-4} \right) \langle p_{k-1} | A | p_{k-1} \rangle, \quad (9a)$$

$$\beta_{k} = -\left(\rho_{k}\rho_{k-1}^{-3}\right) \left\langle p_{k-1} | A | p_{k-1} \right\rangle.$$
(9b)

For the above LA-CG algorithm, used for the purpose of the reduction transformation from A to T, it has been previously proven that the residual value, calculated in the CG iterations using the quantities obtained from Eq. (8), is equivalent to the residual value obtained in the pure CG iterations provided that  $V_{k+1}$  are orthogonal matrices. The methods of the CG and LA, therefore, can be tightly coupled together to tridiagonalize a large symmetric and complex sparse matrix very efficiently. The LA-CG algorithm has been successfully utilized to tridiagonalize the stochastic Liouville matrix in the slow-motional regime. Though the matrices V would inevitably lose orthogonality over Lanczos recursions, the effect of losing orthogonality to the SLE-based lineshape calculations was found to be minor in most of the previous applications.<sup>11</sup> We emphasize that the Lanczos vectors, by losing orthogonality, would cause a deviation of the calculated norm [Eq. (8)] from the genuine values. As a result, the backtransformed eigenvector set (i.e., O, composed from V and O') loses orthogonality as well. It is apparent that these unwanted effects would become greater with increased LA projections.

However, there are limitations for the reduction and diagonal transformations using the LA-CG procedure described above. The generated Lanczos vectors are orthogonal in exact arithmetic; whereas, in finite arithmetic the orthogonality of the Lanczos vectors could be lost easily and quickly because numerical round-off errors accumulate and then spoil the recursions dramatically. We found that these unwanted effects easily become dominant in high-frequency spectral simulations, since the required number of the LA projections increase with the experimental operating frequency. [Though reorthogonalizing the whole set of the Lanczos vectors is a potential cure to this intrinsic drawback of the Lanczosbased methods, it is considered to be impractical because huge amounts of computation time are required for the reorthogonalization task.] In simulating high-frequency and slow-motional spectrum, we found that the LA-CG procedure would typically stagnate and result in breakdown due to the loss of orthogonality in the LA vectors as the Lanczos projections become large in number. The results of the numerical experiments showing this stagnation are illustrated later in Results [cf. Fig. 2]. The stagnation is due to the fact that the amplitude of the calculated residual norm [i.e.,  $\rho$  in Eq. (8)] approaches the computer's allowed round-off error. If we ignore the decreasing  $\rho$ 's and let the LA recursions go on, the tridiagonal matrix [whose elements are calculated from the values of  $\rho$ 's using Eqs. (6)] will give a distorted matrix deviating from the genuine one. If too many Lanczos projections are implemented, the loss of orthogonality (i.e., the elements of  $\mathbf{V}_i^{tr} \mathbf{V}_i$  deviate significantly from zero for  $i \neq j$ ) would dominate the residual norms and gradually destroy the whole LA-CG procedure.

To sum up, the loss of orthogonality participates in the residual norm in two parts: one via the  $\mathbf{V}_{k+1}^{tr}\mathbf{V}_{k+1}$  term, the other via the elements of the tridiagonal matrix calculated using Eqs. (9). As losing orthogonality becomes serious the tridiagonal matrices generated using Eqs. (9) are no longer close to that calculated using Eqs. (6). The elements in the former matrices are contaminated successively and iteratively



FIG. 2. The breakdown in the LA-CG and the cure to the procedure by the LA-QMR.

because the quantities of the  $\rho$ 's [Eqs. (9a) and (9b)] are spoiled by the loss of the orthogonality. The benefits of the computational efficiency brought in by tightly coupling LA with CG become a fatal factor to the LA-CG method as it is used for a very large sparse matrix requiring a large number of Lanczos projections. This is particularly true when one calculates a very slow-motional spectrum at high frequency that requires a large number of Lanczos projections in order to adequately obtain good eigenvalues to display the excellent anisotropic spectral resolution.

#### 2. LA-QMR algorithm

The QMR algorithm was originally developed to be a linear equation solver.<sup>18</sup> It is generally used along with the LA to solve a linear equation system. We, in the following, propose to utilize the LA-QMR to determine the reduced size of the sparse complex symmetric matrices, analogous to the use of the LA-CG shown above.

The LA-QMR differs from the LA-CG in that a least-squares solution is obtained from the Krylov subspace by minimizing the QMR norm  $||\langle J_k | J_k \rangle||$  [cf. Eq. (10)] over  $|y_k\rangle$  [cf. Eq. (8b)] rather than the CG functional over  $|x\rangle$  [cf. Eq. (8)]. Here

$$|J_k\rangle = w_1\beta_1 |e_1\rangle - W_{k+1}\tilde{T}_k |y_k\rangle.$$
<sup>(10)</sup>

In Eq. (10)  $W_{k+1}$  is a positive diagonal weight matrix with the diagonal elements,  $\{w_1, w_2, \ldots, w_{k+1}\}$ . It clearly appears that the QMR iterations depend on the choice of the weighting factors  $w_j$ . One of the common settings for W is the norm

of the Lanczos vector ( $\|\langle v_k | v_k \rangle \|$ ) so that all basis vectors [cf. Eq. (11b)] are corrected to have unit length even as they would otherwise lose normalization due to round-off error in the Lanczos projections. This QMR minimization is the same as in the generalized minimal residual (GMRES),<sup>18</sup> except that the Arnoldi algorithm is replaced with the LA. The minimization of the QMR norm is performed by decomposing the tridiagonal matrix, returned from the LA recursions, with the QR factorization to compute the vector  $|y_k\rangle$ . Hence, the residual norm used to monitor the LA recursions is calculated from Eq. (11a)

$$\left\| r_{k}^{QMR} \right\| = \left( \left| J_{k} \left| U_{k+1}^{tr} U_{k+1} \right| J_{k} \right) \right)^{1/2}$$
(11a)

$$U_{k+1} \equiv V_{k+1} W_{k+1}^{-1}.$$
 (11b)

We emphasize the significant improvement due to the introduction of the weight matrix below. We found that the weight matrix effectively reduces the effect of losing orthogonality in Lanczos vectors as the number of the LA recursion steps becomes large. Compared with the approach of full reorthogonalization on the Lanczos vectors in every iteration, the LA-QMR provides an inexpensive cure for the LA-CG breakdown at a very inexpensive cost. The tridiagonal matrices produced in the LA-QMR iteration are different from that in the LA-CG procedure. In the LA-CG procedure, the diagonal and subdiagonal elements of the triadiagonal matrix are, respectively, calculated from Eqs. (9a) and (9b). In performing reduction transformation of regular matrices, the LA-CG and LA-QMR produce similar tridiagonalized matrices. As the size of the matrix keeps increasing, the number of the LA projections increases, resulting in the fact that the loss of orthogonality occurs in the two algorithms differently, and therefore, the differences between the tridiagonalized matrices of the two methods increase. In our proposed LA-QMR procedure, the tridiagonal matrices are constructed using Eqs. (6a) and (6b). The QMR norms [Eq. (10)] are used as a substitute for the minimal residual norm of CG to monitor the convergence condition. The serious breakdown [cf. Fig. 2] that leads to an infinite iteration loop, which is caused by the stagnation in the CG residual norms, in the LA-CG procedure is, therefore, relieved by the LA-QMR. The numerical experiments of the tests are provided in the following section.

#### **III. NUMERICAL EXPERIMENTS AND DISCUSSION**

#### A. Eigenvector orthogonality is better maintained in the LA-QMR than the LA-CG recursions

To make comparisons of the results of the LA-CG and LA-QMR methods, we performed some numerical experiments. We generated a sparse, symmetric, complex matrix **A** whose dimension is 2000 by 2000. The sparsity of the matrix was 0.3, which indicates 30% of the matrix entries are nonzeros. The matrix **A** was tridiagonalized, followed by the calculations of the eigenvalues using the QL method. The calculated eigenvalues were then examined with the identification test. The whole process is detailed in Fig. 1. Figure 2 shows the results of the orthogonal transformations on the

given matrices A obtained in the procedures, LA-CG (dotted lines) and LA-QMR (solid lines), respectively. The relative norms indicate the ratio of each norm value over that of the first LA step. Figure 2(a) shows that after ca. 280 LA recursion steps the LA-CG procedure stagnated and the relative norms did not decrease any further with the LA projections, whereas the LA-QMR procedure went on until the 534th LA projection reached the convergence criterion, which was ca.  $10^{-27}$  in this case study. Figure 2(b) shows the results of another matrix A (with full dimension of 3000 by 3000). The LA-CG procedure broke down after about the 500th LA step; whereas, the projections in the LA-QMR procedure went on until reaching the convergence criterion at the 994th LA step. The decreasing values of the relative norms as a function of the increasing LA projection step in the LA-OMR procedure provide the required information for us to monitor the LA iterations. Additionally, we would like to point out that as shown in Figs. 2(a) and 2(b) the QMR relative norms do not necessarily converge more rapidly than do the CG norms during the earlier stages. This observation is contrary to the previous results elsewhere.<sup>18</sup> The convergence rate of an iterative method varies with the nature of the target matrix in problem. In addition to the rates of the convergence, we computed the orthogonalities [cf. Eq. (2)] of the orthogonal transformation eigenvectors **O**. The orthogonality<sup>16</sup> ( $\kappa$ ) of a matrix (e.g., **O**) is defined by the Frobenius norm of  $(I - O^{tr}O)$ , where I represents an Identity matrix

$$\kappa \equiv \left\| \mathbf{I} - \mathbf{O}^{\mathrm{tr}} \mathbf{O} \right\|_{F}.$$
 (12)

Note that the matrices **O**'s are obtained by the backtransformation using the Lanczos vectors **V** and the eigenvectors (**O**') of the good eigenvalues that diagonalize the tridiagonal matrices **T**, as illustrated in Fig. 1. The  $\kappa$ 's for the LA-CG and LA-QMR procedures of Fig. 2(a) were 126 and 10<sup>-13</sup>, respectively. The  $\kappa$  values for Fig. 2(b) were 420 and 3.7 for the LA-CG and LA-QMR procedures, respectively. The orthogonalities for the **O** matrices obtained from the LA-QMR are remarkably smaller than those from the LA-CG calculations.

The numerical experiments suggest some improvements that we can make with the LA-QMR algorithm in simulating slow-motional ESR spectrum of high frequency. The key to the success of the SLE-based slow-motional and highfrequency spectral simulations is that an adequate number of the LA projections must be performed before the dominant eigenvalues (i.e., those whose real parts are close to zero) converge, provided that the loss of orthogonality of the O matrix is not substantial. Inadequate steps of the Lanczos projections result in a cascade of damage to the whole calculation. First of all, some of the eigenvalues of T calculated using the QL method would not achieve a satisfactory accuracy and, therefore, would not be identified as good ones in the Cullum-Willoughby process if the Lanczos projections were inadequate. Inadequate Lanczos projections would also produce some spurious eigenvalues. It is worthy to note that the Cullum-Willoughby method does not attempt to identify all eigenvalues that have converged; instead, it is to identify those bad ones and keep all remaining eigenvalues, which may or may not have converged, as good ones. It, therefore, is essential to perform adequate steps of the LA projections before the small but dominant eigenvalues come out. Those eigenvalues, which have not converged or are intrinsically spurious but have not been identified due to the insufficient Lanczos projections, would lead to (1) very slow convergence in calculating eigenvectors using the Inverse Iteration; and (2) producing eigenvectors, which correspond to those less accurate eigenvalues, to be a part of the simulated spectrum.

One convenient way to test whether or not the number of the Lanczos projections is sufficient for the SLE-based calculations of the given dynamical condition is to compare the spectra calculated in two-pulse COSY versus three-pulse ELDOR (with mixing time T<sub>m</sub> set to be zero) modes. Theoretically, a three-pulse ELDOR spectrum, when simulated by setting  $T_m = 0$ , is very close to a two-pulse COSY spectrum, provided that the eigenvector set **O** is absolutely orthogonal [cf. Eq. (3)]. The ELDOR spectral calculations require two orthogonal transformations, respectively, for off-diagonal and diagonal subspaces, while the COSY requires only the former. For the off-diagonal subspace, an inadequate number of LA projections would result in spurious eigenvalues as well as the inaccuracy in the outcome that is to be used for the starting vector for the diagonal subspace. For the diagonal subspace, the same reason can cause the inaccurate eigenvalues and the increase of the unwanted magnitude of the signal (see the  $OO^{tr}$  term in Eq. (3)) contributed from the effect of losing orthogonality. Therefore, the difference between the COSY versus ELDOR at  $T_m = 0$  spectra provides useful information to monitor the unwanted effect due to the loss of orthogonality on O. A large number of Lanczos projections are critically necessary for all good eigenvalues to converge to simulate the slow-motional 2D-ELDOR spectra, particularly the high-frequency ESR spectra. The LA-QMR is developed for such extreme conditions.

# B. Near rigid-limit spectral simulations of W-band 2D-ELDOR experiments

Figure 3(a) shows the 95 GHz (W-band) 2D-COSY spectrum for  $R_0 = 10^6 \text{ s}^{-1}$  obtained in the LA-QMR procedure. The simulated 2D-COSY spectrum from the LA-CG procedure using the same given parameters is displayed in the inset, which apparently appears as distorted lineshapes. The numbers of the iterated LA projections for the two COSY spectra in Fig. 3(a) are 375 and 563, respectively, for the LA-CG and LA-QMR procedures. For the given condition, the LA-CG collapsed as the number of the projections is (approximately) greater than 400. Therefore, we considered the spectrum in the inset of Fig. 3(a) as a distorted and unconverged one. The respective resulting  $\kappa$  values are 101.6 (LA-CG) and 1.3 (LA-QMR). The distorted lineshapes (cf. inset) are the results of the inaccurate eigenvalues, which are due to the inadequate numbers of the LA projections in the LA-CG procedure, and, partly, the effect of losing orthogonality on O. Figure 3(b) displays the slices along the autopeaks of the COSY and ELDOR (at  $T_m = 0$ ) spectra, obtained from the LA-QMR procedure. The spectra of the two modes are alike though the intensities of the autopeaks for the ELDOR are generally weaker than the COSY. The ELDOR experiments for  $T_m = 0$  are experimentally equivalent to the COSY experiments. However, in



FIG. 3. (a) The 2D-COSY spectrum for  $R_0 = 10^6 \text{ s}^{-1}$  simulated using the LA-QMR and the LA-CG (inset). (b) The slices along the autopeaks for the spectra of 2D-COSY and 2D-ELDOR. (c) The 2D-COSY spectrum for  $R_0 = 10^5 \text{ s}^{-1}$  simulated using the LA-QMR. (d) The autopeak slices for 2D-COSY and 2D-ELDOR. The lineshapes are plotted to have the same maximum intensity. (e) The plots of the autopeak slice for the  $R_0 = 10^5 \text{ s}^{-1}$  study as a function of LA projections. It clearly illustrates that having a large and adequate number of the LA projections is crucial to the convergence of the fine details of the slow-motional high-frequency 2D-ELDOR lineshape.

such an extremely slow-motional case the effect of losing orthogonality on **O** begins to gradually develop [via the  $O_0O_0^{tr}$ term in Eq. (3b)] and affect the signal intensity of the calculated ELDOR spectrum. By marking the g values used for the simulations, Fig. 3(b) clearly shows that the lineshapes are not yet the rigid-limit. They, however, did converge. The convergence of the lineshape calculations was examined by comparing the spectra in Fig. 3(b) with the spectra simulated with additional 100 LA projection steps. It is considered as converged when the two calculations, i.e., *m* versus (*m* + 100) LA steps, result in the same (or very similar) spectral lineshapes. Additionally, to completely remove the effect of losing orthogonality from such an extreme case, we suggest carrying out standard Gram–Schmidt (GS) orthogonalization<sup>26</sup> on the diagonal subspace matrix  $O_0$ . The amount of computation time increased substantially (by 6–10 times) using GS, but the resulting spectra for the COSY and ELDOR modes agree very well with the results obtained by the LA-QMR procedure for this case. Note that the dimension of  $O_0$ ,  $N \times m'$ , is much smaller than that of the Lanczos matrix  $V_0$ ,  $N \times m$ , since  $m' \ll m$ . After normalizing the COSY and the reorthogonalized ELDOR spectra, the autopeak slices of the two spectra were found to overlap completely.

Figures 3(c) and 3(d) show the simulation results for  $R_0 = 10^5 \text{ s}^{-1}$  in the LA-QMR procedure. The convergence was confirmed. The iterated LA projections are 412 and 633, respectively, for the spectra of the COSY and ELDOR modes. The peak in the higher frequency [cf. Fig. 3(c)] is much bet-

ter revealed as the  $R_0$  is decreased by an order of magnitude, compared to Fig. 3(b). Figure 3(d) clearly shows the rigid-limit lineshapes for  $R_0 = 10^5 \text{ s}^{-1}$  at 95 GHz. In the W-band range, the anisotropic property of the g tensors is clearly revealed and separated. The dashed lines represent the anisotropic g values given to the simulations. The peak locations of the simulated lineshapes are in good agreement with the given values. The COSY versus ELDOR spectra display very similar rigid-limit lineshapes. It suggests an adequate number of the LA projections performed in the simulations. Again, the autopeak slices in Fig. 3(d) were obtained without performing GS orthogonalization on matrix  $O_0$ . It is clearly shown in Figs. 3(b) and 3(d) that the dissimilarity in the autopeak slices of the COSY versus ELDOR spectra is indeed increased with a decrease in the rotational diffusion time. The dissimilarity could be easily corrected by performing GS orthogonalization on  $O_0$ , whereas at the cost of computation time. Figure 3(e) shows the autopeak slices of the ELDOR spectra for  $R_0 = 10^5 \text{ s}^{-1}$  [i.e., the study in Figs. 3(c) and 3(d)] as a function of LA projections. In this extremely slow-motional case, the lineshape converged slowly requiring a large number of LA projections. The lineshape varied with the LA projections and did not converge until the number of the LA projections was greater than ca. 600. The calculation of 800 LA projections confirms the convergence of the lineshape. Overall, the result indicates that monitoring the LA projections via the residuals is crucial to obtaining a converged 2D-ELDOR lineshape, which requires a large and adequate number of the LA projections for the eigenvalues and eigenvectors to converge.

#### IV. SUMMARY AND CONCLUSIONS

High-field/high-frequency ESR experiments provide a much better orientational resolution than those at conventional frequency to reveal the dynamics on the spectral lineshapes. Because of the excellent spectral resolution of the experimental spectra, high-field cw-ESR has, in recent years, been demonstrated as a powerful tool to decompose the dynamics of proteins into various dynamic modes through theoretical lineshape analysis. In the present report, we have made a significant further improvement on the numerical algorithm required for the lineshape analysis of high-frequency 2D-ESR. The new numerical algorithm is an improved version of the Lanczos-based methods for performing the orthogonal transformation of the stochastic Liouville superoperator matrix, which is large, but sparse, symmetric, and non-Hermitian. We have demonstrated that by replacing the CG with the QMR in the Lanczos recursions, the orthogonal transformation and associated tri-diagonal matrix, which are greatly reduced in dimension from the original, are found to better represent the original sparse matrix than does that obtained from the LA-CG. The criterion upon which this statement is made is largely based on the observed convergence of the 2D-ESR spectra calculated from the respective eigenvalues and eigenvectors. The LA-QMR relieves the unwanted effects caused by the loss of orthogonality in Lanczos recursions so that it is able to allow a larger number of the Lanczos projections than does the LA-CG. We, therefore, are able to obtain the eigenpairs to better accuracy. In the very slowmotional regime ( $R_0 = 10^5 \sim 10^6 \text{ s}^{-1}$ ), reorthogonalization of the reduced diagonal sub-space matrix might still be necessary in order to completely remove the unwanted magnitude of the 2D-ELDOR signal contributed from the effect of losing orthogonality. The improvement provided by LA-QMR has been demonstrated to be particularly critical for simulating the slow-motional lineshapes at high frequency, which display high orientational resolution.

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