

Notes on Direct Simulation Methods for Electron Paramagnetic Resonance Spectra

Keith A. Earle

Physics Department

University at Albany

1400 Washington Ave, Albany, NY 12222

October 8, 2008

Abstract

Direct simulation methods of Electron Paramagnetic Resonance (EPR) spectra are an alternative to standard eigenfunction-based approaches. Both methods can be employed to find numerical solutions of the Stochastic Liouville Equation (SLE) in order to compute spectral lineshapes. It can be shown rigorously that the domain of validity of eigenfunction expansion solutions of the SLE covers only a limited range of parameter space. Although the computed spectrum in the linear response regime may appear ‘reasonable’, the eigenvectors and eigenvalues of the matrix representation of the spectral resolvent are only approximately correct. This is a serious issue for the accurate representation of time domain experiments, where the eigenvalues and eigenvectors must be known precisely. With the advent of time-domain experiments at high fields on fluid systems, the breakdown of standard eigenfunction expansions is more acute. It is clear that a more accurate method of spectral simulation is needed to address these issues. Direct simulation of the spectra from a time series of molecular orientations does not suffer from the defects of eigenfunction expansion methods and may be usefully combined with state of the art molecular dynamics simulations both in the linear response regime and in the non-linear response regime.

1 Introduction

The Stochastic Liouville Equation (SLE) allows one to compute ensemble properties of spin dynamics in systems subject to stochastic relaxation processes. [1] Shortly after its introduction, Freed and coworkers greatly extended the range of applicability of the SLE by removing certain unnecessary restrictions and introducing an eigenfunction expansion approach as a practical method of solution. [2] Independently of the eigenfunction expansion approach developed by Freed and coworkers, methods of direct simulation based on Monte Carlo evaluation of a path-integral like formulation were also explored. The work by Pedersen is typical of this alternative approach and is noteworthy due to its emphasis on the importance of proper sampling for accurate spectral simulation. [3] Due to the efficiency with which the required matrix elements could be computed in the eigenfunction expansion method compared to the relatively more computationally intensive direct simulation methods, given the computer hardware available at the time, direct simulation methods fell into disfavor.

Improvements in computer hardware led to the implementation of automated non-linear least squares fitting of EPR spectra in fluid domains for frequency-domain and time-domain experiments [4] once the eigenfunction method was extended to account quantitatively for time-domain (pulse) experiments. [5] The eigenfunction method was also developed to handle models of stochastic processes of increasing complexity. [6] Applications of the eigenfunction expansion approach to quantitative spectral analysis of high field and multifrequency EPR data sets represent some of the most demanding computational challenges in the field of EPR lineshape analysis, due to the superior orientational resolution of high field EPR spectra and its sensitivity to diffusion model. [7, 8]

Given the evident success of the eigenfunction method it seemed that its range of application could be pushed to apparently arbitrary limits. Little work was done to verify this perception, or quantify its domain of validity. The eigenfunction expansion of the SLE results in a matrix representation of the coupled reorientational and spin degrees of freedom. It is not clear *a priori* how faithful such a matrix representation is of the underlying differential equation. The secular g-tensor problem is a useful testbed for exploring these questions, as the eigenfunctions and eigenvalues of the equivalent Sturm-Liouville problem can be found exactly. [9] In addition, the matrix represen-

tation of the SLE for the secular g-tensor problem is tridiagonal and thus the eigenfunctions and eigenvectors of the spectral resolvent can be determined in a very straightforward manner. [10]

Work done in the mathematical physics community suggested that the domain of validity for eigenfunction expansions of second order differential equations, even for the secular g-tensor problem, was smaller than commonly supposed. [11] One particularly unnerving feature of Redparth's work was the strong dependence of the asymptotic spectrum of a non self-adjoint operator, the relevant case for the lineshape problem due to the stochastic relaxation term, on an arbitrarily small fixed perturbation. For spectral simulations depending on accurate eigenvalues and eigenvectors, such as time-domain experiments, particularly at high field, where orientational selectivity requires large basis sets, it seems prudent to ask if spectral simulation methods that do not rely on eigenfunction expansions might be usefully pressed into service.

With the advent of fast, cheap, computational hardware, it seemed worthwhile to reinvestigate the path-integral approach. The increasing sophistication of molecular dynamics calculations also kindled early interest in computing spectra from MD trajectories. [12] One of the major issues attendant on time-stepping the dynamics is that the spin Hamiltonian does not commute at different times. Different workers deal with this matter in different ways. Westlund and coworkers pointed out that many of the commonly used approximations were not norm preserving and thus subject to significant, cumulative errors for long trajectories. [13] Westlund and coworkers were able to show that by partitioning the Liouville operator properly, a norm-preserving representation of the propagator could be computed at each time step. [13, 14] In order to obtain a calculable representation of the propagator at each time step, the symmetrized form of the Trotter expansion due to Suzuki is applied. [15] The particular partitioning chosen by Westlund and coworkers allows one to rewrite the propagator at each time step as a product of exponentials that can be rewritten in terms of sines and cosines with matrix coefficients. There is one matrix that is diagonal that has a trivial exponential. These properties follow from the special symmetries of the matrices chosen for the partitioning such that even powers are all equal, up to integer powers of a scalar, and all odd powers are also equivalent up to integer powers of a scalar. The even powers can all be combined into a term proportional to $\cos \theta - 1$. The odd powers can be combined into a term proportional to $\sin \theta$. [13, 14]

This approach, although elegant, relies on careful orchestration of special symmetries in the problem. No algorithm is provided for nuclear spins higher than $I = 1$ and the submatrix of the Liouville operator studied by Westlund and coworkers restricts applications to the linear response regime. One of the goals of this work is to relax these restrictions and achieve a more flexible and general formalism.

2 Equation of Motion

We begin with the Liouville-von Neumann equation which quantifies the time dependence of the spin density matrix $\rho(t)$ under the action of a time dependent Hamiltonian $\mathcal{H}(t)$.

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} [\mathcal{H}(t), \rho(t)] \quad (1)$$

The Hamiltonian may be partitioned into terms that depend on applied static magnetic fields leading to time-independent terms that define the energy levels in the system. The remaining terms in the Hamiltonian will be, in general, time dependent and will induce transitions between the energy levels defined by the time independent terms. The time dependent perturbations are of two kinds: coherent representing the effects of applied rf or mmw fields, and incoherent due to stochastic relaxation processes. The latter may be derived from MD time series, if available, or by other means such as modeling a random walk in orientation space. Although one can work directly with Equation 1 there are advantages to using a formalism which allows one to follow the time dependence of transitions, as these are the quantities of interest in spectroscopy. In this case, we need a mapping of the density matrix $\rho(t)$ treated as a state vector in transition space into itself. We may define the superoperator

$$\mathcal{L}(t) = [\mathcal{H}(t), E_{S \otimes I}] \quad (2)$$

where $E_{S \otimes I}$ is a unit matrix with the same (square) dimension as $\mathcal{H}(t)$. The subscript $S \otimes I$ explicitly indicates the common situation that there is a significant hyperfine coupling. Using Equation 2, we can rewrite Equation 1 in the following form

$$\frac{\partial \rho(t)}{\partial t} = -\frac{i}{\hbar} \mathcal{L}(t) \rho(t) \quad (3)$$

where $\boldsymbol{\rho}(t)$ is now a state vector in transition space.

When the dynamics of $\boldsymbol{\rho}(t)$ are treated in this fashion it is important to note that the dimensions of $\mathcal{L}(t)$ are much larger than those of $\mathcal{H}(t)$. For example, a single spin 1/2 electron is described by a 2×2 Hamiltonian matrix. The \mathcal{L} operator associated with this Hamiltonian is 4×4 . For the case of one spin 1/2 electron coupled *via* a hyperfine coupling to a spin one nucleus, modeling a nitroxide, the matrix representation of \mathcal{L} is 36×36 . Some care is needed to avoid losing one's way in a sea of indices. One must also choose an ordering for the elements of $\boldsymbol{\rho}(t)$ taken as a state vector. In some sense, the actual ordering is immaterial, as they are all equivalent up to an orthogonal similarity transformation. Nevertheless, a particular choice can often highlight underlying symmetries in the problem. Considerations such as these guided Westlund and coworkers to the choice made in their publications. We will use a somewhat different ordering, based on the p and q indices introduced by Freed and coworkers. [16] For ease of comparison, we will derive the orthogonal transformation required to translate between the two approaches.

Equation 2 can be expressed in standard tensor operator form as follows

$$\mathcal{L}(t) = \mathcal{H}(t) \otimes E_{S \otimes I} - E_{S \otimes I} \otimes \mathcal{H}(t)^T \quad (4)$$

Here the notation T indicates the transpose operation and \otimes indicates the Kronecker tensor product. This definition of $\mathcal{L}(t)$ induces a natural ordering of the elements of $\boldsymbol{\rho}(t)$ which we will call 'Kronecker ordering'. For the case of a nitroxide, we have azimuthal quantum numbers $m_S = \pm 1/2$ and $m_I = \{1, 0, -1\}$. Taking the electron azimuthal index first, the first row of the upper left-most six by six block of \mathcal{L} in Kronecker ordering is column-indexed as follows

$$[1/2, 1/2; 1, 1], [1/2, 1/2; 1, 0], [1/2, 1/2; 1, -1], [1/2, -1/2; 1, 1], [1/2, -1/2; 1, 0], [1/2, -1/2; 1, -1] \quad (5)$$

In terms of the p and q indices introduced by Freed and coworkers this can be rewritten, using the order $[p^S, q^S; p^I, q^I]$, as

$$[0, 1; 0, 2], [0, 1; 1, 1], [0, 1; 2, 0], [1, 0; 0, 2], [1, 0; 1, 1], [1, 0; 2, 0] \quad (6)$$

where $p^S = m'_S - m''_S$, $q^S = m'_S + m''_S$, $p^I = m'_I - m''_I$ and $q^I = m'_I + m''_I$. Note that with Kronecker ordering, the different p^S and q^S sub-spaces are mingled. It is convenient to group the $p^S = 1$

$p^S = 0$ and $p^S = -1$ subspaces together in order to follow the dynamics more easily. We show the required orthogonal transformations in the appendix. Westlund and coworkers consider the $p^S = 1$, $q^S = 0$ subspace, which corresponds to the linear response regime. [17] It is important to recall that the operator \mathcal{L} maps transitions, so one must specify both row and column transition indices in order to follow the evolution of a particular transition. In the linear response regime, convention dictates that one follows the evolution of the $p^S = 1$ subspace, so for this case, one would select all rows and columns with $p^S = 1$. For a nitroxide, this generates a nine by nine matrix of coupled *nuclear* transitions. This submatrix is constructed by truncating the Hamiltonian so that only secular terms depending on $S_z \otimes I_z$ and pseudosecular terms depending on $S_z \otimes I_{\pm}$ are retained. By working with a formalism that retains all contributions to the Liouville operator \mathcal{L} it is possible to examine critically and quantitatively when contributions to the Hamiltonian may be truncated.

3 Matrix Elements of the Liouville Operator

The procedure for constructing the spin Hamiltonian as contractions of irreducible spherical tensor operators has been carefully reviewed elsewhere. [18] In the lab frame, one may show for the hyperfine interaction that

$$\begin{aligned} \langle p_1^S, q_1^S; p_1^I, q_1^I | [A_{A,L}^{(l,m)}]^\times | p_2^S, q_2^S; p_2^I, q_2^I \rangle = \\ \Delta(m, \Delta p; |\Delta p^S|, |\Delta q^S|; |\Delta p^I|, |\Delta q^I|; \Delta p^S \Delta p^I, \Delta q^S \Delta q^I) (-1)^{\Delta p[l]} \\ \times \begin{pmatrix} 1 & 1 & l \\ \Delta p^S & \Delta p^I & -\Delta p \end{pmatrix} S_A \end{aligned} \quad (7)$$

where

$$\begin{aligned} \Delta(m, \Delta p; |\Delta p^S|, |\Delta q^S|; |\Delta p^I|, |\Delta q^I|; \Delta p^S \Delta p^I, \Delta q^S \Delta q^I) = \\ \delta_{m, \Delta p} \delta_{|\Delta p^S|, |\Delta q^S|} \delta_{|\Delta p^I|, |\Delta q^I|} \delta_{\Delta p^S \Delta p^I, \Delta q^S \Delta q^I} \end{aligned} \quad (8)$$

and the quantities $[l] = \sqrt{2l+1}$, $\Delta p^S = p_1^S - p_2^S$, $\Delta q^S = q_1^S - q_2^S$, $\Delta p^I = p_1^I - p_2^I$ and $\Delta q^I = q_1^I - q_2^I$. The quantity S_A is transition index dependent and takes the following values

$$S_A = \begin{cases} (p_1^S q_1^I + p_1^I q_1^S)/2 & \text{if } \Delta p^S = 0, \Delta p^I = 0 \\ -(p_1^S \Delta p^I + q_1^S \Delta q^I) K_I / \sqrt{8} & \text{if } \Delta p^S = 0, \Delta p^I \neq 0 \\ -(p_1^I \Delta p^S + q_1^I \Delta q^S) / \sqrt{8} & \text{if } \Delta p^S \neq 0, \Delta p^I = 0 \\ \Delta p^S \Delta q^I K_I / 2 & \text{if } \Delta p^S \neq 0, \Delta p^I \neq 0 \end{cases} \quad (9)$$

The notation used here follows Lee, *et al.* [5] Here, the superscript \times indicates a superoperator. Note that the subscripts 1 refer to the relevant row of \mathcal{L} and the subscripts 2 refer to the relevant column of \mathcal{L} . Similarly, for the electron Zeeman interaction, one has

$$\begin{aligned} & \langle p_1^S, q_1^S; p_1^I, q_1^I | [A_{g,L}^{(l,m)}]^\times | p_2^S, q_2^S; p_2^I, q_2^I \rangle = \\ & \Delta(m, \Delta p; |\Delta p|, |\Delta q|; \Delta p^I, 0; \Delta q^I, 0) B_0 (-1)^{\Delta p [l]} \\ & \times \begin{pmatrix} 1 & 1 & l \\ \Delta p & 0 & -\Delta p \end{pmatrix} \left(p_1^S \delta_{\Delta p^S, 0} - \Delta q^S (1 - \delta_{\Delta p^S, 0}) / \sqrt{2} \right) \end{aligned} \quad (10)$$

The nuclear Zeeman term, when needed, may be treated along the lines given in Lee, *et al.* [5].

In order to include the effect of time varying coherent perturbations, we must augment the expressions we have written down for the Zeeman interaction with additional terms accounting for the presence of transverse rf or mmw fields. Longitudinal fields can be accommodated by a straightforward extension of the expressions given above. A linearly polarized rf, or millimeter wave, magnetic field along the Laboratory x-axis with time dependence $\cos(\omega t - \phi)$ has the following representation in terms of irreducible spherical tensor operators (ISTO)

$$T_{B_{1,L}}^{(1,\pm 1)} = \mp \frac{B_1}{\sqrt{2}} \cos(\omega t - \phi) \quad (11)$$

When contracted with the electron spin operator S expressed as an ISTO one can construct a spin superoperator as outlined by Freed and coworkers. [16] Since the procedure is only outlined in reference [16] and there are some confusing typos in that presentation, it is worthwhile to go through the steps of an explicit construction.

The ISTO representation of a spin J operator is

$$T_J^{(1,\pm)} = \mp \frac{J_{\pm}}{\sqrt{2}} \quad (12)$$

$$T_J^{(1,0)} = J_z \quad (13)$$

which has the following matrix elements in a basis labeled by azimuthal quantum numbers

$$\langle m_J^1 | T_J^{(1,m)} | m_J^2 \rangle = \delta_{m_J^1, m_J^2} \left(m_J^1 \delta_{m,0} - m \delta_{|m|,1} [J(J+1) - m_J^1 m_J^2]^{1/2} / \sqrt{2} \right) \quad (14)$$

In order to construct the superoperator representation of a spin operator, we must compute the matrix elements of the following Kronecker tensor products $T_J^{(1,m)} \otimes E_J$ and $E_J \otimes [T_J^{(1,m)}]^T$. The bras and kets for this tensor product depend on two azimuthal quantum numbers, defining a transition.

The matrix elements are defined as

$$\langle m'_1, m''_1 | T_J^{(1,m)} \otimes E_J | m'_2, m''_2 \rangle \equiv \langle m'_1 | T_J^{(1,m)} | m'_2 \rangle \langle m''_1 | E_J | m''_2 \rangle \quad (15)$$

where we have suppressed the explicit J dependence. We have chosen to express the superoperator matrix elements in terms of a general operator J instead of S or I in order to have results that can be applied to EPR, ELDOR or ENDOR if desired. It is useful to express the azimuthal quantum numbers in terms of the p and q indices introduced above. One finds

$$m'_1 = \frac{p_1^J + q_1^J}{2} \quad (16)$$

$$m''_1 = \frac{q_1^J - p_1^J}{2} \quad (17)$$

$$m'_2 = \frac{p_2^J + q_2^J}{2} \quad (18)$$

$$m''_2 = \frac{q_2^J - p_2^J}{2} \quad (19)$$

The matrix elements of the identity operator E_J degenerate into Kronecker delta functions. For example

$$\langle m''_1 | E_J | m''_2 \rangle = \delta_{\frac{q_1^J - p_1^J}{2}, \frac{q_2^J - p_2^J}{2}} \quad (20)$$

which implies the following algebraic relation

$$\frac{q_1^J - p_1^J}{2} = \frac{q_2^J - p_2^J}{2} \quad (21)$$

which may be used to rearrange the Kronecker delta in Equation 20 into the equivalent form

$$\langle m_1'' | E_J | m_2'' \rangle = \delta_{\Delta p^J, \Delta q^J} \quad (22)$$

where $\Delta p^J = p_1 - p_2$ and $\Delta q^J = q_1 - q_2$.

Similar considerations apply to computing the matrix elements of $T_J^{(1,m)}$. One finds

$$\langle m_1' | T_J^{(1,m)} | m_2' \rangle \equiv \left\langle \frac{p_1^J + q_1^J}{2} \left| T_J^{(1,m)} \right| \frac{p_2^J + q_2^J}{2} \right\rangle \quad (23)$$

$$= \delta_{\Delta p^J, m} \left[\delta_{\Delta p^J, 0} \left(\frac{p_1^J + q_1^J}{2} \right) - \delta_{|\Delta p^J|, 1} \Delta p^J \frac{K_J}{\sqrt{2}} \right] \quad (24)$$

where $K_J = [J(J+1) - (q_1^J \Delta q_1^J + p_1^J \Delta p_1^J)(q_1^J \Delta q_1^J + p_1^J \Delta p_1^J - 2)/4]^{1/2}$. Note that the factor K_J comes from the raising and lowering operators in T_J . In order to put K_J in this form it is helpful to use the identity $(\Delta p^J)^2 = (\Delta q^J)^2$ where the equality is enforced by the Kronecker delta functions imposed by the matrix elements of E_J . It is useful to note some special cases. For $J = 1/2$, $K_{1/2} = 1$. For $J = 1$, $K_1 = \sqrt{2}$. For larger values of J , K_J depends on q_1^J . Note that for transverse excitation fields, we need only retain the K_J dependent term in Equation 24

The other contribution to the superoperator requires a little more care

$$\langle m_1', m_1'' | E_J \otimes [T_J^{(1,m)}]^T | m_2', m_2'' \rangle \equiv \langle m_1' | E_J | m_2' \rangle \langle m_2'' | T_J^{(1,m)} | m_1'' \rangle \quad (25)$$

Note carefully the interchange of bra and ket in the last factor of Equation 25 due to the transpose operation on LHS of Equation 25. In terms of the p and q indices one finds

$$\langle m_2'' | T_J^{(1,m)} | m_1'' \rangle = \delta_{\Delta p^J, m} \left[\delta_{\Delta p^J, 0} \left(\frac{q_1^J - p_1^J}{2} \right) - \delta_{|\Delta p^J|, 1} \Delta p^J \frac{K_J}{\sqrt{2}} \right] \quad (26)$$

In terms of the p and q indices, the superoperator matrix elements relevant for transverse excitation fields will depend on the K_J dependent terms of Equations 24 and 26. With due care for the sign of Δp^J appearing in the relevant terms, the result can be simplified as follows

$$\langle p_1^J, q_1^J | [T_J^{(1,m)}]^\times | p_2^J, q_2^J \rangle = -\delta_{|\Delta p^J|, |\Delta q^J|} \delta_{\Delta p^J, m} \delta_{|\Delta p^J|, 1} \frac{\Delta q^J}{\sqrt{2}} \quad (27)$$

What appears in the expression for the excitation Liouville superoperator is the contraction of $[T_J^{(1,m)}]^\times$ with the appropriate components of Equation 11. In addition, the resultant of the contraction of the ISTO representation of the transverse field(s) with the spin J can be further

contracted with a coupled spin F . For example, a nuclear spin $I = F$ coupled to an electron spin $S = J$ via hyperfine coupling, will generate a typical term in the electron excitation Liouville superoperator of the form $\left[T_{B_{1,L}}^{(1,m_B)} \otimes \left[T_J^{(1,m_J)} \right]^\times \right] \otimes T_F^{(0,0)}$. The factor $T_F^{(0,0)}$ contributes products of delta functions when matrix elements of the excitation Liouville operator are computed. Putting the pieces together, the electron excitation Liouville superoperator in the high field limit has the following matrix elements

$$\langle p_1^S, q_1^S; p_1^I, q_1^I | [l] \begin{pmatrix} 1 & 1 & l \\ -1 & 1 & 0 \end{pmatrix} T_{B_{1,L}}^{(1,\pm 1)} \otimes \left[T_S^{(1,\mp 1)} \right]^\times \otimes T_F^{(0,0)} | p_2^S, q_2^S; p_2^I, q_2^I \rangle = -T_{B_{1,L}}^{(1,\pm 1)} \Delta (|\Delta p^S|, |\Delta q^S|; \Delta p^S, \mp 1; |\Delta p^S|, 1; \Delta p^I, \Delta q^I; \Delta p^I, 0) \frac{\Delta q^S K_S}{\sqrt{2}} \quad (28)$$

As an example of the kinds of terms that contribute to the secular part of the Liouville operator, Figure 1 shows the nuclear Zeeman term.

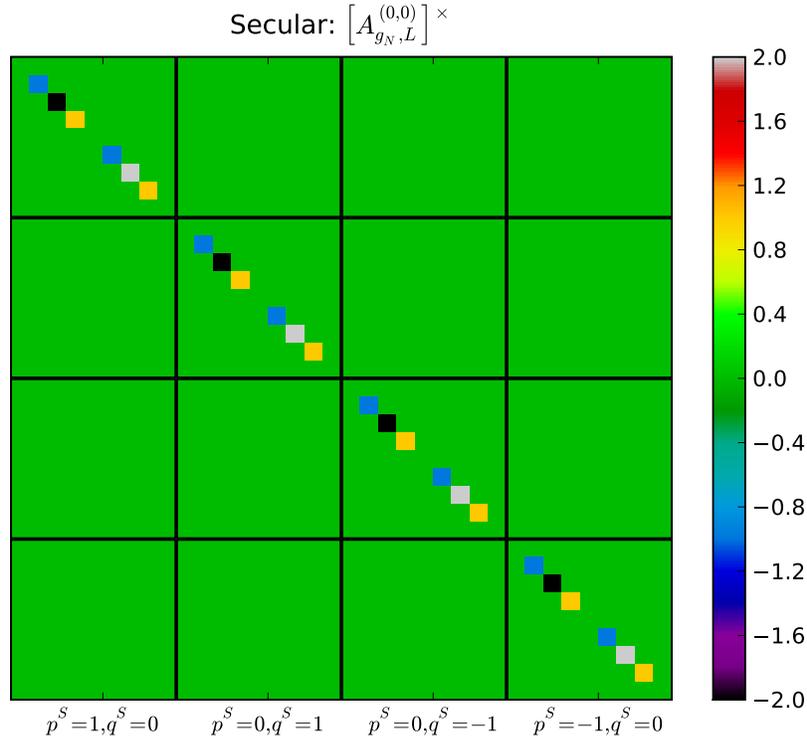


Figure 1: Plot of the Nuclear Zeeman contributions to the Liouville operator

As discussed in Schneider and Freed [18], however, the ISTOs corresponding to the g tensor

take their simplest form when referred to a body-fixed coordinate system. In the principal axis system (PAS) of the g tensor, one finds

$$F_{g,M}^{(0,0)} = -\frac{1}{\sqrt{3}} \left(\frac{\beta_e}{\hbar} \right) (g_{xx} + g_{yy} + g_{zz}) \quad (29)$$

$$F_{g,M}^{(2,0)} = \sqrt{\frac{2}{3}} \left(\frac{\beta_e}{\hbar} \right) \left(g_{zz} - \frac{1}{2} (g_{xx} + g_{yy}) \right) \quad (30)$$

$$F_{g,M}^{(2,\pm 2)} = \frac{1}{2} \left(\frac{\beta_e}{\hbar} \right) (g_{xx} - g_{yy}) \quad (31)$$

where the subscript M indicates that the tensor components are referred to the PAS of the g-tensor. In the presence of an ordering potential or significant tilts in the system, one requires, in general, the machinery of Wigner rotation matrices to transform the tensor components expressed in the molecular PAS to the laboratory PAS.

Another interesting case is the effect of the modulation field on the spectrum, where a time-dependent term proportional to $\mathbf{B}_{mod}(t) = B_{mod}(t)\hat{z}$ is significant. This has recently become significant for high field high frequency EPR within the context of frequency modulation EPR [19]. The case of ELDOR and ENDOR can also be treated by the techniques outlined here. For the present purpose, we will limit attention to the scalar terms in the saturation hamiltonian for one applied rf field, corresponding to the most important case in practice. Extensions to more general cases involve difficulties of detail, not principle.

4 Transformation to the Lab Frame

In writing down the Hamiltonian operator it is noteworthy that the spin operators take their simplest form when expressed in the lab frame. The magnetic ‘tensors’ take their simplest form in a body-fixed principal axis system. In order to compute the tensor contractions appearing in the expression for the Hamiltonian [18]

$$H(\Omega) = \sum_{\mu,m,l} (F_{\mu,\eta}^{(l,m)})^* A_{\mu,\eta}^{(l,m)} = \sum_{\mu,m,l} (-1)^m F_{\mu,\eta}^{(l,-m)} A_{\mu,\eta}^{(l,m)}, \quad (32)$$

where the index μ indicates the interaction, *e.g.*, Zeeman or hyperfine, η specifies the relevant frame, body-fixed or space-fixed, and l and m indicate the ISTO tensor indices. As discussed in Schneider

and Freed, [18] the relevant values of l are 0 and 2 for many problems in magnetic resonance. The $l = 0$ terms take a particularly simple form

$$H_0 = \sum_{\mu} F_{\mu,L}^{(0,0)} A_{\mu,L}^{(0,0)}, \quad (33)$$

where L indicates that both terms are evaluated in the space-fixed lab frame. This notation makes use of the observation that $T^{(0,0)}$ is orientation independent and may therefore be transformed to an arbitrary frame by relabeling, as done here. The journey for the $l = 2$ terms is a little more arduous. For the situation where there is a tilt ϕ of the magnetic ‘tensors’ with respect to the principal axis system of the diffusing molecule, and a tilt ψ of the nematic ordering axis with respect to the applied static field the relevant transformation may be written in the conventional Euler angle formulation as follows

$$H_1(\Omega) = \sum_{\mu,m',m'',m'''} \mathcal{D}_{m,m'}^2(0, \psi, 0) \mathcal{D}_{m',m''}^2(\alpha(t), \beta(t), \gamma(t)) \mathcal{D}_{m'',m'''}^2(0, \phi, 0) F_{\mu,M}^{(2,m''')} A_{\mu,L}^{(2,m)}, \quad (34)$$

where the index M indicates that $\{F_{\mu,M}^{(2,m''')}\}$ are evaluated in the magnetic tensor frame. As written, Equation 34 does not allow for a tilt between the Zeeman and hyperfine principal axis systems. It is straightforward to augment Equation 34 with this additional transformation when needed. It is seldom relevant for nitroxide spin label work.

Although the Euler angle parameterization is familiar, it is not the most useful parameterization of the rotations required to transform from body-fixed to space-fixed axes when individual time steps must be followed. See Section 6 for further discussion on this point. For the standard lineshape calculation in terms of eigenfunction expansions, the parameterization is immaterial, as all orientations are averaged over. Thus, the ambiguities of the Euler angle parameterization [21, 22] do not affect the results. When individual time steps are important, as in the present calculation, the quaternion parameterization offers the most reliable way forward. [20] Altmann provides a prescription for converting from an Euler angle parameterization to a parameterization known as the Euler-Rodrigues parameters. See Section 6 for details, particularly Equation 42. In terms of the Euler-Rodrigues parameters, the Wigner rotation matrix element may be computed as follows [23]

$$\mathcal{D}_{m',m}^j(a, b) = [(j+m')!(j-m')!(j+m)!(j-m)!]^{1/2} \sum_k \frac{a^{j+m-k} (a^*)^{j-m'-k} b^{m'-m+k} (-b^*)^k}{(j+m-k)!(j-m'-k)!(m'-m+k)!k!}, \quad (35)$$

where the sum over k is restricted to those values that render the arguments of the factorials in Equation 35 non-negative, and

$$a = \lambda - i\Lambda_z, a^* = \lambda + i\Lambda_z, b = -i(\Lambda_x - i\Lambda_y), b^* = i(\Lambda_x + i\Lambda_y). \quad (36)$$

In terms of the Euler-Rodrigues parameters, the Wigner rotation matrix elements $\mathcal{D}_{m',m}^2$ may be written as follows

$\mathcal{D}_{m',m}^2(a,b)$	$m = 2$	$m = 1$	$m = 0$	$m = -1$	$m = -2$
$m' = 2$	a^4	$-2a^3b$	$\sqrt{6}a^2b^2$	$2ab^3$	b^4
$m' = 1$	$-2a^3(b^*)$	$a^2(1 - 4b(b^*))$	$-\sqrt{6}ab(1 - 2b(b^*))$	$-(1 - 4a(a^*))b^2$	$2(a^*)b^3$
$m' = 0$	$\sqrt{6}a^2(b^*)^2$	$-\sqrt{6}a(b^*)(1 - 2b(b^*))$	$1 - 6a(a^*)b(b^*)$	$\sqrt{6}(a^*)b(1 - 2b(b^*))$	$\sqrt{6}(a^*)^2b^2$
$m' = -1$	$-2a(b^*)^3$	$-(1 - 4a(a^*))(b^*)^2$	$-\sqrt{6}(a^*)(b^*)(1 - 2b(b^*))$	$(a^*)^2(1 - 4b(b^*))$	$2(a^*)^3b$
$m' = -2$	$(b^*)^4$	$-2(a^*)(b^*)^3$	$\sqrt{6}(a^*)^2(b^*)^2$	$2(a^*)(b^*)^3$	$(a^*)^4$

The \mathcal{D} functions satisfy a number of useful identities, among which the following was used to verify the entries in the table above: $(\mathcal{D}_{m',m}^l)^* = (-1)^{m'-m}\mathcal{D}_{-m',-m}^l$. When $\alpha = \gamma = 0$, which occurs in the transformation of the F functions when there is a director tilt ψ or diffusion tilt ϕ , the a and b parameters degenerate into the following forms $a = a^* = \lambda = \cos \frac{\beta}{2}$, $b = -b^* = -\Lambda_y = -\sin \frac{\beta}{2}$, which corresponds to a rotation by the angle β around the y-axis. In this case the $\mathcal{D}_{m',m}^2$ functions degenerate into the ‘reduced’ Wigner rotation matrices $d_{m',m}^2$ and the general expression for the Hamiltonian, Equation 34, reduces to that given in Schneider and Freed.[18] Tables of the reduced Wigner rotation matrices are given in many places. We cite the two used in this work.[24, 25]

5 A Useful Operator Identity

In order to solve Equation 3 we need to be able to compute expressions of the form $\exp[-it\mathcal{L}(t)/\hbar]$. The basic problem is that in general $[\mathcal{L}(t'), \mathcal{L}(t'')] \neq 0$ if $t' \neq t''$ due to the stochastic modulation of the spin operators in \mathcal{L} . The Suzuki-Trotter expansion can be applied to a succession of time steps, but the success of the method depends on being able to calculate matrix exponentials efficiently, while enforcing the unitary condition on the propagator. Westlund and coworkers achieved this by restricting attention to the linear response problem and choosing a matrix partitioning scheme that allowed for fast and accurate computation of the matrix exponentials appearing in the Suzuki

Trotter decomposition. As noted in the introduction, the matrix decomposition developed by Westlund and coworkers resulted in a finite sum involving the unit operator and calculable matrices with trigonometric prefactors. It is not known to us how much further this technique can be extended in a practical sense. Fortunately, there exists an alternative approach, based on a remark by Gilmore, that may easily be extended to spins higher than $S = 1/2$ and $I = 1$ and results in finite sequences of matrices for which the matrix elements are easy to calculate. [26]

The basic approach is to take the Suzuki Trotter decomposition as applied by Westlund and coworkers and repartition the Hamiltonian from which the Liouville superoperator is constructed into upper triangular, lower triangular, and diagonal pieces for each time step. The diagonal contribution is trivial to exponentiate. The Taylor series expansion of the upper and lower triangular matrices will terminate in a finite number of steps thus reducing the computation of a transcendental matrix function to an algebraic one. Although it is a straightforward though tedious exercise to verify these statements explicitly, it is useful to have a general operator identity that allows one to abstract away the details of a particular representation so that general statements may be made.

The first observation is that it is possible to compute powers of Equation 4 with the help of the following identity [27]

$$(A \otimes B)(C \otimes D) = (AC) \otimes (BD) \quad (37)$$

where the square matrix representation of the operators A , B , C , and D all have the same dimension. If we define $H^0 = E$ then we can write the n^{th} power of \mathcal{L} in terms of a generalization of the binomial theorem

$$\mathcal{L}^n = \sum_{k=0}^n \binom{n}{k} (H)^{n-k} \otimes (-H^T)^k \quad (38)$$

Proof: by induction. Note that the Hamiltonian may itself be written as a Kronecker product of operators. For example, the Hamiltonian of a spin S electron coupled to a spin I nucleus can be written as $H = H_S \otimes H_I$. Thus, by Equation 37, $H^n = H_S^n \otimes H_I^n$. The transpose contribution to \mathcal{L} requires a bit more care. Note that under the Kronecker product $H^T = H_S^T \otimes H_I^T$. Thus

$$(H^T)^n = (H_S^T)^n \otimes (H_I^T)^n \quad (39)$$

by repeated application of Equation 37. Substituting these results into Equation 38 we find

$$\mathcal{L}^n = \sum_{k=0}^n \binom{n}{k} [H_S^{n-k} \otimes H_I^{n-k}] \otimes [(H_S^T)^k \otimes (H_I^T)^k] (-1)^k \quad (40)$$

We are now in a position to make some general statements about how many non-vanishing powers of \mathcal{L} we can expect for various partitionings of the Hamiltonian. It is still useful to resolve the Hamiltonian and thus the Liouville superoperator into secular, pseudosecular and nonsecular contributions. The secular contributions to H are diagonal and may be treated by elementary methods. The pseudosecular contributions contain terms of the form $S_z \otimes I_{\pm}$. All powers of S_z are non-vanishing, so if the pseudosecular contributions to the Liouville superoperator propagator have an algebraic representation, it must come from I_{\pm} . Note that a generic pseudosecular term in \mathcal{L}^n will depend on $(I_{\pm})^{n-k} \otimes [(I_{\pm}^T)^k]$. However, for spin I , the maximum number of times that I_+ or I_- may be applied sequentially is $2I$. Thus the highest allowed value of n for pseudosecular terms is $4I$, as we can have $2I$ powers of I_{\pm} and $2I$ powers of (I_{\pm}^T) . Alternatively, note that $n - k = k = 2I$ requires $n = 4I$. For non-secular terms in the presence of a hyperfine interaction, the constraint on the allowed number of terms is set by the smaller of S or I . For doublet EPR, the limit is set by $S = 1/2$. Thus we observe that for doublet EPR the non-secular contributions to the Liouville superoperator truncate after two terms.

As an example of what this looks like in practice, Figure 2 shows a typical non-secular term proportional to $S_+ I_z$.

The Liouville operator for this term, squared, has the following matrix representation, shown in Figure 3

Given the structure of the matrix shown in Figure 3, it is clear that higher powers must vanish. At this point, it is useful to note that the figures showing the matrix representation of the various contributions to the Liouville operators have been plotted in dimensionless units, so that they may be plotted on comparable scales. For nitroxide spectra, the electron Zeeman and hyperfine contributions become comparable at 35 GHz, corresponding to an applied field of 1.2 T. At 95 GHz, the nuclear Zeeman contributions are comparable to the A_y component of the hyperfine tensor. These scaling relationships should be borne in mind when comparing Figures 1–3. One point worth noting is that the $m = 0$ contributions to the Liouville operator need to be partitioned into

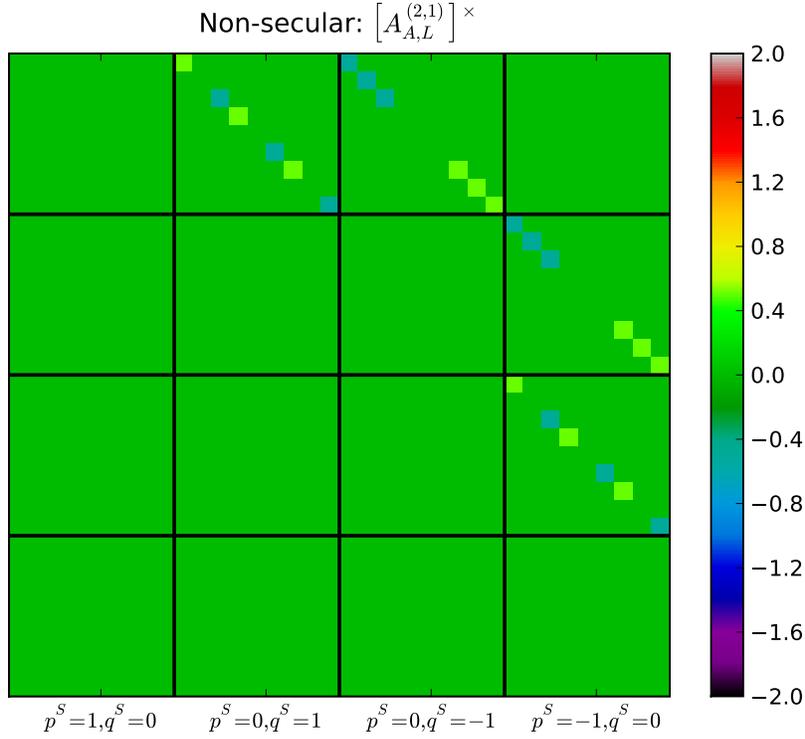


Figure 2: Plot of the non-secular Hyperfine $l = 2$, $m = 1$ contribution to the Liouville operator S_+I_- and S_-I_+ terms in order to avoid complicated representations of $\exp(-it\mathcal{L}^{(l,0)}(t)\Delta t)$ in terms of products of sines and cosines with a non-trivial time dependence and a set of calculable but non-intuitive matrices.

Figure 4 shows a matrix representation of the $l = 2$, $m = 0$ contribution of the hyperfine interaction to the Liouville operator.

Note that the ‘flip-flop’ and ‘flop-flip’ contributions are symmetrically disposed about the main diagonal. Although higher powers have a repeating structure, from which a representation in terms of $\sin n\theta$ and $1 - \cos n\theta$ may be computed where $n = 1, 2$ and $\theta = \omega t$ where ω is a characteristic frequency, the results are not particularly useful. Figure 5 shows a representation of $(\mathcal{L}^{(2,0)})^2$. Note that the pattern of relative magnitudes is more complex in Figure 5 than in Figure 4. As mentioned above, although it is possible to find a closed form expression for the infinite sequence implied by $\exp(-i\mathcal{L}^{(2,0)}t)$, it is not particularly useful.

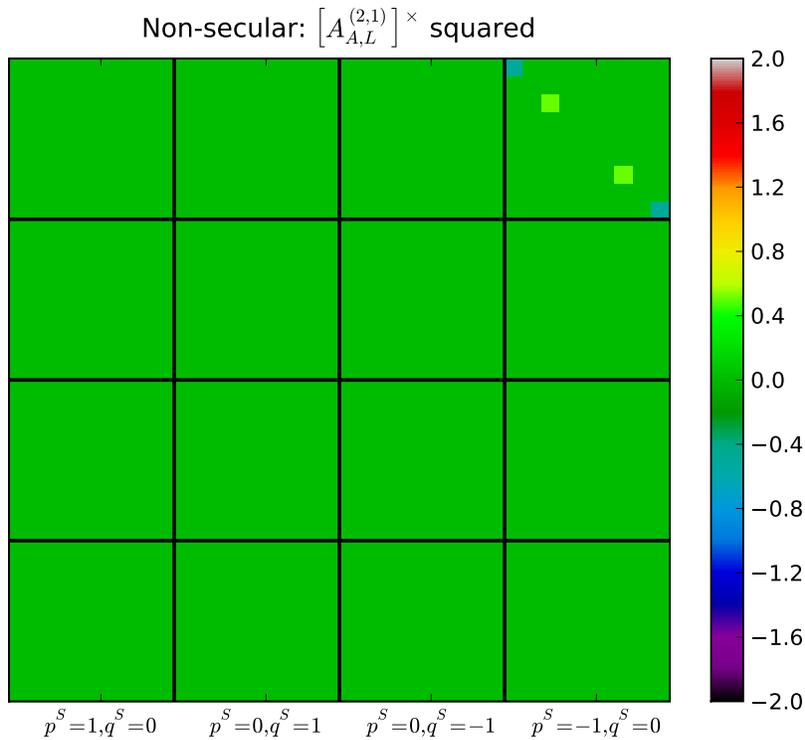


Figure 3: Plot of the non-secular Hyperfine $l = 2$, $m = 1$ contribution to the Liouville operator, squared

6 Rigid Body Dynamics from the Quaternion Perspective

In order to model the stochastic relaxation process that determines the details of the lineshape in the path integral formulation, we require a time series of orientations obtained from a molecular dynamics calculation, or by some other means. In order to keep this work reasonably self-contained, we will model the stochastic relaxation process as a random walk through orientation space. Since the required time series are long, especially for high field EPR spectra it is important to have a representation of rotations that is stable and non-singular. It has been known for a long time that the default choice of tracking orientations via Euler angles is fraught with error.[21, 22] An alternative parameterization, closely related to the quaternion calculus, is provided by the so-called Euler-Rodrigues (ER) parameters.[28] We shall not have to use many detailed properties of quaternions. The book by Altmann provides sufficient background for the current application.[20]

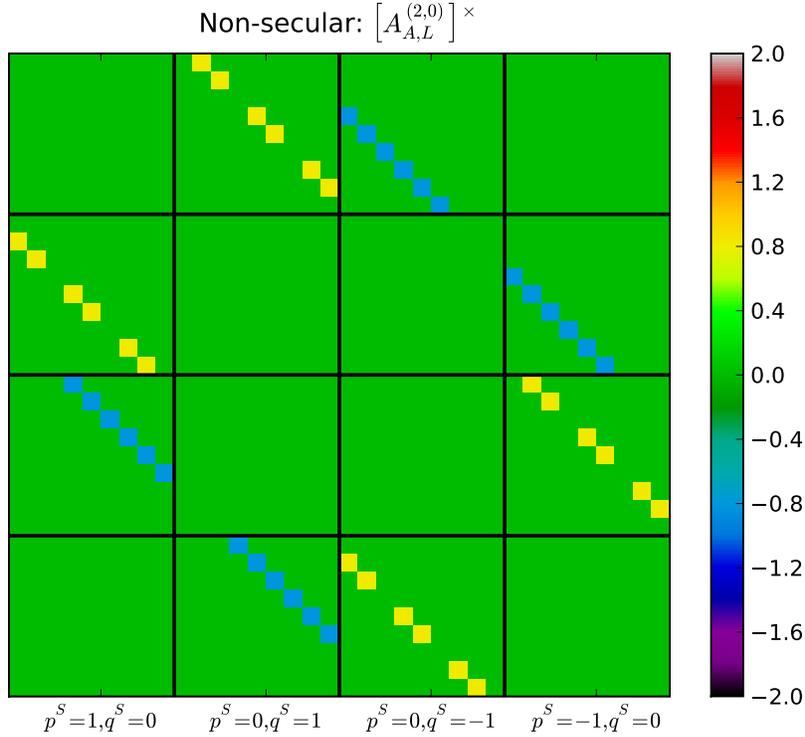


Figure 4: Plot of the non-secular Hyperfine $l = 2$, $m = 0$ contribution to the Liouville operator.

When the (ER) parameterization is chosen, describing rotations by quaternions allows one to write a very compact expression for the time evolution of the ER parameters [28]

$$\dot{\epsilon} = \frac{1}{2}\Omega\epsilon. \quad (41)$$

Here, ϵ is a quaternion parameterizing the rotation expressed in Euler angles as follows [20]

$$\epsilon = \begin{bmatrix} \lambda \\ \Lambda_x \\ \Lambda_y \\ \Lambda_z \end{bmatrix} \equiv \begin{bmatrix} \cos \frac{\beta}{2} \cos \frac{1}{2}(\alpha + \gamma) \\ -\sin \frac{\beta}{2} \sin \frac{1}{2}(\alpha - \gamma) \\ \sin \frac{\beta}{2} \cos \frac{1}{2}(\alpha - \gamma) \\ \cos \frac{\beta}{2} \sin \frac{1}{2}(\alpha + \gamma) \end{bmatrix}. \quad (42)$$

The quantity ϵ satisfies the normalization condition $(\epsilon)^{Tr}\epsilon = 1$, as one may show from the parameterization in terms of Euler angles given in Equation 42. The quantity Ω is a skew-symmetric

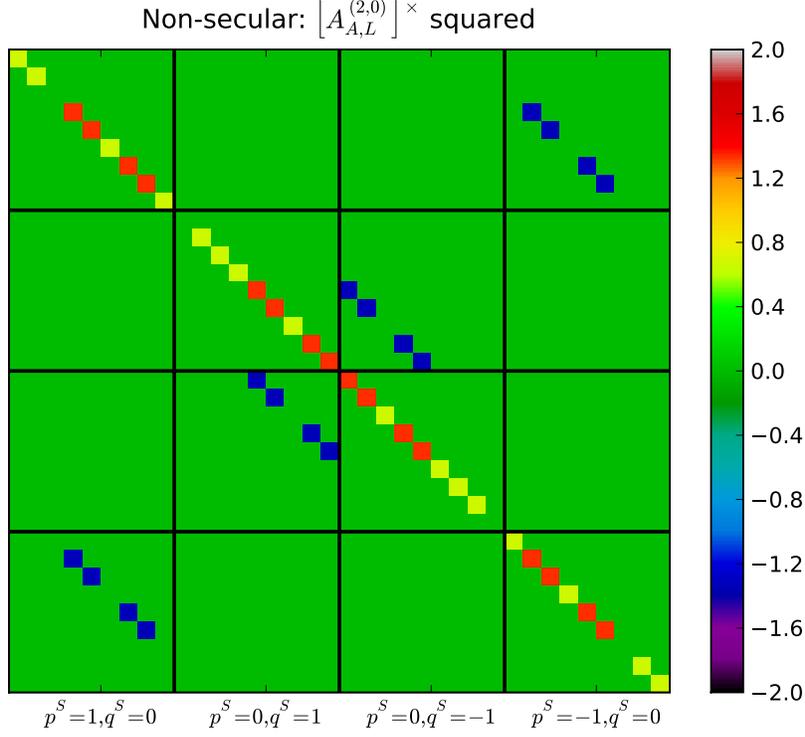


Figure 5: Plot of the non-secular Hyperfine $l = 2$, $m = 0$ contribution to the Liouville operator, squared

matrix of the instantaneous angular velocities [28]

$$\Omega = \begin{pmatrix} 0 & -\omega_x & -\omega_y & -\omega_z \\ \omega_x & 0 & \omega_z & -\omega_y \\ \omega_y & -\omega_z & 0 & \omega_x \\ \omega_z & \omega_y & -\omega_x & 0 \end{pmatrix}. \quad (43)$$

Note that Ω has the following properties $\Omega + (\Omega)^{Tr} = 0$ and $\Omega (\Omega)^{Tr} = -(\omega_x^2 + \omega_y^2 + \omega_z^2)^2 E_4$. For a random walk through orientation space Ω will be a function of time, thus Equation 41 cannot be integrated easily for all times. For long time trajectories it will be useful to enforce a normalization condition on ϵ . Any iterative solution of Equation 41 will not satisfy the normalization condition unless the generator of time translation itself has unity norm. From the properties of Ω it is clear that this is not the case. However, for sufficiently short time scales, one may write down a solution

of Equation 41 that does preserve the norm. Over a time Δt short compared to the time scale over which Ω varies appreciably one may write in the lab frame

$$\epsilon(t + \Delta t) = \exp\left(\frac{\Delta t}{2}\Omega(t)\right) \epsilon(t). \quad (44)$$

Defining the quantity $p = \sqrt{\omega_x^2 + \omega_y^2 + \omega_z^2}$ one may rewrite the matrix exponential appearing in Equation 44 as follows

$$\exp\left(\frac{\Delta t}{2}\Omega(t)\right) = \cos\left(p\frac{\Delta t}{2}\right) E_4 + \sin\left(p\frac{\Delta t}{2}\right) \frac{1}{p}\Omega(t). \quad (45)$$

This equation defines an orthogonal transformation $\exp(\Omega\Delta t/2)^{-1} = \exp\left((\Omega(t))^{Tr} \Delta t/2\right)$. Using the properties of Ω given above, one may verify that $\exp(\Omega\Delta t/2) \exp\left((\Omega(t))^{Tr} \Delta t/2\right) = 1$. Given that the transpose operation defines the matrix representation of the quaternion norm $(\epsilon(t))^{Tr}\epsilon(t) = 1$, it is trivial to show that if $\epsilon(t)$ is normalized, then $\epsilon(t + \Delta t)$ is normalized if the time translation operator $\exp(\Omega\Delta t/2)$ is used. A similar result is given in Siminovitch for the case of a constant Ω matrix. [28] It should be remembered that the result given here is only valid for time steps Δt short enough that $\Omega(t)$ does not vary appreciably during the time step. This is similar in spirit to the way the time slicing was done in Westlund's approach to discretizing the solution of the SLE. [13]

Now that we have a way of ensuring that the quaternion representing the rotation at each time step is normalized, we may consider the problem of computing the angular velocities at each time step. The Euler equations may be written in the form

$$I_\alpha \dot{\omega}_\alpha = \tau_\alpha + (I_\beta - I_\gamma)\omega_\beta\omega_\gamma \quad (46)$$

when the subscripts on ω are taken in cyclic order.[29] Here, I_α is one of the eigenvalues of the inertia tensor in the principal axis system and τ_α is a component of the external torque. Omelyan then shows that the n^{th} iteration of the equations of motion for ω may be written as follows

$$\omega_\alpha^{(n)}(t+\Delta t) = \omega_\alpha(t) + \frac{\Delta t}{2I_\alpha} \left[\tau_\alpha(t) + \tau_\alpha(t + \Delta t) + (I_\beta - I_\gamma)(\omega_\beta(t)\omega_\gamma(t) + \omega_\beta^{(n-1)}(t + \Delta t)\omega_\gamma^{(n-1)}(t + \Delta t)) \right], \quad (47)$$

where the iteration index $n = 1, 2, \dots$, and $\omega_\alpha^{(0)}(t + \Delta t) = \omega_\alpha(t)$. Based on MD simulations of a TIP4P model of water, it was found that only a small number of iterations were required to get accurate, updated ω values.[29]

References

- [1] Kubo, R. “Stochastic Theories of Randomly Modulated Systems” in “Proceedings of the International Conference on Statistical Mechanics (1968)” *J. Phys. Soc. Japan* 26(supp):1–5 (1969)
- [2] Freed, J. H., G. V. Bruno and C. F. Polnaszek, “Electron Spin Resonance Line Shapes and Saturation in the Slow Motional Region” *J. Phys. Chem.* 75(22):3385–3399
- [3] Pedersen, J. B. “Monte Carlo Calculation of ESR Lineshapes in the Slow Motional Region”, *J. Chem. Phys.* 57(7):2680–2683
- [4] Budil, D. E., S. Lee, S. Saxena and J. H. Freed. “Non-linear Least-Squares Analysis of Slow-Motion EPR Spectra in One and Two Dimensions Using a Modified Levenburg-Marquardt Algorithm” *J. Magn. Reson.* A120:155–189 (1996)
- [5] Lee, S., D. E. Budil and J. H. Freed “Theory of two-dimensional Fourier transform electron spin resonance for ordered and viscous fluids” *J. Chem. Phys.* 101(7):5529–5558 (1994)
- [6] Polimeno, A. and J. H. Freed “A Many-Body Stochastic Approach to Rotational Motions in Liquids” *Adv. Chem. Phys.* 83:89–201 (1992)
- [7] Earle, K. A., D. E. Budil and J. H. Freed “250 GHz-EPR of Nitroxides in the Slow-Motional Regime: Models of Rotational Diffusion” *J. Phys. Chem.* 97(50):13289–13297 (1993)
- [8] Earle, K. A. and D. E. Budil “Calculating Slow-Motion ESR Spectra of Spin-Labeled Polymers” in “Advanced ESR Methods in Polymer Research”, S. Schlick, Ed. Wiley (New York, 2006)
- [9] Flammer, C. Spheroidal Wave Functions. Stanford, CA: Stanford University Press, 1957.
- [10] Moro, G. and U. Segre “Ultraslow Motions and Asymptotic Lineshapes in ESR” *J. Magn. Reson.* 83:65–78 (1989)

- [11] Redparth, P. “Spectral Properties of Non-self-adjoint Operators in the Semi-classical Regime” *J. Diff. Eq.* 177:307330 (2001)
- [12] Robinson, B. H., L. J. Slutsky and F. P. Auteri “Direct Simulation of Continuous Wave Electron Paramagnetic Resonance Spectra from Brownian Dynamics Trajectories” *J. Chem. Phys.* 96(4):2609–2616 (1992)
- [13] Håkansson, P., P. O. Westlund, E. Lindahl and O. Edholm “A direct simulation of EPR slow-motion spectra of spin labelled phospholipids in liquid crystalline bilayers based on a molecular dynamics simulation of the lipid dynamics” *Phys. Chem. Chem. Phys.* 3:5311–5319 (2001)
- [14] Usova, N. P.O. Westlund, and I. I. Fedchenia “Direct simulation of slow-motion electron spin resonance spectra by solving the stochastic Liouville equation in the time domain with stochastic dynamics in the form of trajectories” *J. Chem. Phys.* 103(1):96–103 (1995)
- [15] Suzuki, M. “Convergence of General Decompositions of Exponential Operators” *Commun. Math. Phys.* 163:491–508 (1994)
- [16] Meirovitch, E. D. Igner, E. Igner, G. Moro and J. H. Freed “Electron-spin relaxation and ordering in smectic and supercooled nematic liquid crystals” *J. Chem. Phys.* 77(7):3915–3938 (1982)
- [17] Schneider, D. J., and J. H. Freed “Spin Relaxation and Motional Dynamics” in “Lasers, Molecules and Methods”, J. O. Hirschfelder, R. E. Wyatt and R. D. Coalson, Eds. *Adv. Chem. Phys.* 73:387–527 (1989)
- [18] Schneider, D. J., and J. H. Freed “Calculating Slow Motional Magnetic Resonance Spectra: A User’s Guide” in “Biological Magnetic Resonance”, L. J. Berliner and J. Reuben, Eds. 8:1–76 (1989)
- [19] Hyde J. S., W. Froncisz, J. W. Sidabras, T. G. Camenisch, J. R. Anderson, and R. A. Strangeway. “Microwave frequency modulation in CW EPR at W-band using a loop-gap resonator”, *J. Magn. Reson.*, **185** 259–263 (2007).

- [20] Altmann, S. L. “Rotations, Quaternions and Double Groups” c. 12, Clarendon (Oxford, 1986)
- [21] Evans, D. J. “On the Representation of Orientation Space”, *Mol. Phys.* 34(2):317–325 (1977)
- [22] Lynden-Bell, R. M. and A. J. Stone. “Reorientational Correlation Functions, Quaternions and Wigner Rotation Matrices”, *Molecular Simulation* 3:271–281 (1989)
- [23] Altmann, *ibid.*, c. 14.
- [24] Varshalovich, D. M., A. N. Mosakev and V. K. Khersonskii. “Quantum Theory of Angular Momentum”, c. 4, World Scientific (Singapore, 1988)
- [25] Brink, D. M. and G. R. Satchler. “Angular Momentum” Third Edition, c. 2, App. V, Clarendon, (Oxford, 1993)
- [26] Gilmore, R. “Lie Groups, Lie Algebras, and Some of Their Applications” pp. 153–158, Dover (New York, 2002)
- [27] Gamliel, D. and H. Levanon “Stochastic Processes in Magnetic Resonance” pp. 19–21, World Scientific (Singapore, 1995)
- [28] Siminovitch, D. J. “A Classical View of the Euler Angles and the Euler Kinematic Equations in NMR”, *J. Magn. Reson.* 117A:235-245 (1995)
- [29] Omelyan, I. P. “On the numerical integration of motion for rigid polyatomics: The modified quaternion approach” arXiv:physics/9901028v1 [physics.comp-ph] 18 Jan 1999