Parameter Sensitivity of the Saturated Lineshape

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Abstract

These notes generalize expressions for analytical derivatives derived earlier to the saturated axial g-tensor lineshape case, where the starting vector as well as the matrix representation of the Stochastic Liouville Equation depend on the system parameters. In the present problem, the starting vector is linearly dependent on the strength of the applied rf field. This is a particularly simple parameter dependence. Nevertheless, it is illustrative of many of the features that enter into a careful treatment of problems whose starting vector has a non-linear parameter dependence, such as diffusion in a potential.

1 Introduction

La Beauté

Je suis belle, ô mortels! comme un rêve de pierre,
Et mon sein, où chacun s'est meurtri tour à tour,
Est fait pour inspirer au poète un amour
Eternel et muet ainsi que la matière.

Je trône dans l'azur comme un sphinx incompris;
J'unis un coeur de neige à la blancheur des cygnes;
Je hais le mouvement qui déplace les lignes,
Et jamais je ne pleure et jamais je ne ris.

Les poètes, devant mes grandes attitudes,
Que j'ai l'air d'emprunter aux plus fiers monuments,
Consumeront leurs jours en d'austères études;

Car j'ai, pour fasciner ces dociles amants,
De purs miroirs qui font toutes choses plus belles:
Mes yeux, mes larges yeux aux clartés éternelles!

—Charles Baudelaire

The Stochastic Liouville Equation (SLE) is a powerful tool for studying magnetic resonance lineshapes. In a previous set of notes, the conditions of validity for the SLE were given[1]. There, it was emphasized that the original formulation[2, 3] was intended for the linear response regime. Freed and coworkers extended the range of applicability of the SLE approach to the non-linear response regime by recasting the SLE into a form suitable for studying the time dependence of the density matrix[4]. In order to account for relaxation to the equilibrium density matrix, the following form for the time dependence of the density matrix is assumed[5, 6]

$$\frac{\partial}{\partial t}\chi = \frac{1}{i\hbar}\left[\mathcal{H},\chi\right] + \frac{1}{i\hbar}\left[\mathcal{H},\rho_0\right] - \Gamma\chi, \tag{1}$$

where χ is the deviation of the density matrix from its equilibrium value, $\chi = \rho - \rho_0$. The second commutator on the right hand side of Equation 1 is the source of the so-called starting vector, due to the applied RF field. If non-secular terms are retained in the Hamiltonian, then this term couples the equilibrium spin eigenstates and the rotational eigenstates. These terms are tacitly dropped in earlier treatments[4]. A justification for including the driving term back to equilibrium is given elsewhere[7]. The Hamiltonian consists of orientation independent terms that are assumed to be time independent, stochastic, orientation dependent terms which are *implicitly* time dependent, and *explicitly* time dependent terms which can be written in the following form

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1(\Omega) + \mathcal{H}_2(t). \tag{2}$$

In applications of the SLE to the linear response regime, only $\mathcal{H}_0$ and $\mathcal{H}_1(\Omega)$ in Equation 2 are considered. In the presence of a strong rf field $\mathcal{H}_2$ the full Hamiltonian must be considered. The case treated here will be one of moderate saturation, where any time dependence of ρ_0 due to $\mathcal{H}_2$ will be neglected. Using the methods of Freed and coworkers[4], Equation 1 may be decomposed into an infinite series of Floquet modes under the assumption of the following form for χ

$$\chi \equiv \sum_{n=-\infty}^{\infty} \frac{1}{\sqrt{8\pi^2}} Z^{(n)} \exp(in\omega t), \tag{3}$$

where ω is the frequency of the applied coherent perturbation $\mathcal{H}_2(t)$. The factor of $1/\sqrt{8\pi^2}$ in Equation 3 is for ease of subsequent manipulations. It corresponds to a factor $\sqrt{p_0}$ where $p_0 = 1/8\pi^2$ for isotropic fluids and results from a symmetrization operation on the relaxation superoperator Γ[8, 9]. For moderate saturation, the following Floquet modes are needed $n \in \{-1, 0, 1\}$ for the case $S = 1/2$. Assuming that $\mathcal{H}_2(t)$ is of the following form $2\omega_1 S_x \cos(\omega t)$ where S_x is a spin operator for the electron spin and ω_1 is the strength of the applied field in frequency units, $\mathcal{H}_2(t)$ will couple different Floquet modes. Due to the structure of the SLE[1], χ or equivalently $Z^{(n)}$ will be a product of spin operators and an orientation-dependent term. The orientation-dependent terms may be chosen to be eigenfunctions of the Γ operator, in which case the $\mathcal{H}_1(\Omega)$ operator will couple different Γ eigenfunctions. The $\mathcal{H}_0$ interaction sets the resonant energy for the electron spin ensemble. When non-secular contributions are included in $\mathcal{H}_1(\Omega)$, then $[\mathcal{H}_1(\omega), \mathcal{H}_0] \neq 0$. These terms may be interpreted as stochastic spin torques[8]. For now, only secular perturbations will be included in $\mathcal{H}_1(\Omega)$. The modifications due to non-secular terms will be considered in Section 3.

Under these assumptions, the equation of motion for the n^{th} Floquet mode is

$$\begin{aligned} & in\omega Z^{(n)} + \Gamma Z^{(n)} \\ & \quad -\tfrac{1}{i\hbar} \left(\mathcal{H}_0 + \mathcal{H}_1(\Omega)\right)^{\times} Z^{(n)} - \tfrac{1}{i\hbar}\omega_1 S_x^{\times} \left(Z^{(n-1)} + Z^{(n+1)}\right) \\ & \qquad = \sqrt{8\pi^2}\left(\delta_{n,1} + \delta_{n,-1}\right) \tfrac{\omega_1}{i\hbar} S_x^{\times} \rho_0, \end{aligned} \tag{4}$$

where the superoperator notation $A^{\times}B \equiv [A, B]$ has been used. A leisurely derivation of Equation 4 is given in Gamliel and Levanon[6], which may be consulted for more details. For $S = 1/2$, there are four 'transitions' to keep track of: $++$, $--$, $+-$ and $-+$, where $m_S = 1/2 \rightarrow +$ and $m_S = -1/2 \rightarrow -$. The 'transitions' $++$ and $--$ are populations, and $+-$ and $-+$ correspond to the action of raising and lower operators. One often sees the following mnemonic device[4] for labeling the transitions $+- \equiv \leftarrow$ and $-+ \equiv \rightarrow$. In the linear response regime, the term proportional to ω_1 on the left hand side of Equation 4 may be dropped and then the Floquet modes decouple. It is conventional to retain only the $n = 1$ mode in that case, as the $n = \pm 1$ Floquet modes are related by complex conjugation. For the $n = 1$ mode the $-+$ transition is the one that is relevant for computing the linear response, and this corresponds to the $p^S = -1$ transition index in the notation of Moro and Freed[10]. The $p^S = -1$ index is appropriate for the density matrix formalism given here. In the linear response regime, where one works with the Heisenberg representation, $p^S = 1$ is the appropriate choice as discussed elsewhere[1, 8]. When the saturation term is retained, all

four transitions $ij \in \{+,-\}$ and all relevant Floquet modes $n \in \{-1,0,1\}$ need to be retained in principle, leading to twelve coupled equations of motion for the spin degrees of freedom, even before the effect of $\mathcal{H}_1(\Omega)$ is included. Fortunately, considerable simplifications to the coupled set of equations can be affected, and one can reduce the required set of equations to four. In the secular g-tensor problem, further simplifications allow one to partition the equations of motion so that in the end only two coupled equations remain. In that case, the coupling provided by $\mathcal{H}_1(\Omega)$ is simple enough that insight into the structure of the equations may still be retained. For the non-secular couplings discussed in Section 3, the full set of twelve equations is needed. In the high field and moderate saturation approximations, perturbation theory may be used to again reduce the number of coupled equations to three. Experience with the slow tumbling secular g-tensor model in Section 2, allows one to identify a dynamic frequency shift and broadening due to the non-secular perturbation, as will be seen. Dynamic frequency shifts and broadenings are discussed in some detail in Section 1.2. The dynamic frequency shift is an instance of the *mouvement qui déplace les lignes* which inspired the choice of this section's epigraph.

In what follows, the Einstein summation convention will be assumed (repeated indices are summed over) unless otherwise specified. Taking ij matrix elements of Equation 4 yields

$$\begin{aligned} in\omega Z^{(n)}_{ij} + \Gamma Z^{(n)}_{ij} \\ -\frac{1}{i\hbar}\left[(\mathcal{H}_0)_{ik}Z^{(n)}_{kj} - (\mathcal{H}_0)_{lj}Z^{(n)}_{il}\right] \\ -\frac{1}{i\hbar}\left[(\mathcal{H}_1(\Omega))_{ik}Z^{(n)}_{kj} - (\mathcal{H}_1(\Omega))_{lj}Z^{(n)}_{il}\right] \\ -\frac{\omega}{i\hbar}(S_x)_{ik}\left(Z^{(n-1)}_{kj} + Z^{(n+1)}_{kj}\right) \\ +\frac{\omega}{i\hbar}(S_x)_{lj}\left(Z^{(n-1)}_{il} + Z^{(n+1)}_{il}\right) \quad = \\ (\delta_{n,1} + \delta_{n,-1})\frac{\sqrt{8\pi^2}}{i\hbar}\left[(S_x)_{ik}(\rho_0)_{kj} - (S_x)_{lj}(\rho_0)_{il}\right] \end{aligned} \tag{5}$$

In writing Equation 5, use has been made of the observation that the matrix elements of the spin, Hamiltonian and Z operators are c-numbers and may thus be ordered according to convenience. Note further that states in this transition space are labeled by pairs of indices. In order to make further progress it is useful to have explicit expressions for the matrix elements of S_x, $\mathcal{H}_0$, $\mathcal{H}_1(\Omega)$ and ρ_0. Using the methods reviewed in Schneider and Freed[9], the required matrix elements for the secular g-tensor problem in the high temperature limit are given in Table 1. Note that $g_{\parallel} = g_{zz}$ and $g_{\perp} = (g_{xx} + g_{yy})/2$ in the notation of Schneider and Freed[9]. In addition $\mathcal{D}^2_{00}(\Omega)$ is a Wigner rotation matrix element. It is the stochastic dependence of Ω on time that couples rotational degrees of freedom to the spin degrees of freedom via $\mathcal{H}_1$. Using the notation introduced in Table 1, one obtains four coupled equations of motion for $Z^{(n)}_{ij}$ in the high field and moderate

	$++$	$--$	$+-$	$-+$
S_x	0	0	$\frac{\hbar}{2}$	$\frac{\hbar}{2}$
H_0	$\frac{\hbar\omega_0}{2}$	$-\frac{\hbar\omega_0}{2}$	0	0
$H_1(\Omega)$	$\frac{\hbar\omega_2}{2}\mathcal{D}^2_{00}(\Omega)$	$-\frac{\hbar\omega_2}{2}\mathcal{D}^2_{00}(\Omega)$	0	0
ρ_0	$\frac{p_0}{A}\left(1-\frac{\hbar\omega_0}{2k_BT}\right)$	$\frac{p_0}{A}\left(1+\frac{\hbar\omega_0}{2k_BT}\right)$	0	0

Table 1: Matrix elements for the Secular g-tensor problem. Here $\omega_0 \equiv (1/3)(g_\parallel + 2g_\perp)(\beta_e/\hbar)B_0$, $\omega_2 \equiv (2/3)(g_\parallel - g_\perp)(\beta_e/\hbar)B_0$ and $A = (2S+1)^2$ is the normalization constant of the density matrix in the high temperature limit. The quantity p_0 is the equilibrium orientation distribution. For isotropic fluids $p_0 = 1/8\pi^2$.

saturation approximations:

$$(i(\omega-\omega_0)+\Gamma)Z^{(1)}_{-+} - i\omega_2\mathcal{D}^2_{00}(\Omega)Z^{(1)}_{-+} - id\left[Z^{(0)}_{++} - Z^{(0)}_{--}\right] = idqp_0\sqrt{8\pi^2} \quad (6)$$

$$\Gamma Z^{(0)}_{++} + id\left[Z^{(1)}_{-+} - Z^{(-1)}_{+-}\right] = 0 \quad (7)$$

$$\Gamma Z^{(0)}_{--} - id\left[Z^{(1)}_{-+} - Z^{(-1)}_{+-}\right] = 0 \quad (8)$$

$$(-i(\omega-\omega_0)+\Gamma)Z^{(-1)}_{+-} + i\omega_2\mathcal{D}^2_{00}(\Omega)Z^{(-1)}_{+-} + id\left[Z^{(0)}_{++} - Z^{(0)}_{--}\right] = -idqp_0\sqrt{8\pi^2} \quad (9)$$

In Equations 6–9, the following quantities are introduced: $d \equiv \hbar\omega_1/2$, $q \equiv \hbar\omega_0/Ak_BT$. Given that it is only the difference $Z^{(0)}_{++} - Z^{(0)}_{--}$ that appears in Equations 6 and 9 one may combine Equations 7 and 8 and reduce the number of required equations to three. For isotropic fluids, the factor $p_0\sqrt{8\pi} = \sqrt{p_0}$ as discussed above. The factor $\sqrt{p_0}$ arises from a symmetrization operation on the rotational diffusion operator Γ that is trivial for isotropic fluids, but is essential for rendering the matrix representation of the SLE complex symmetric in the presence of an ordering potential[9]. Note further that the superscript on Z is equal to the negative of the difference of the subscripts $i-j$ with the identification $+ \rightarrow 1/2$, $- \rightarrow -1/2$ noted above. Thus, the Floquet index is redundant in this problem and will be dropped in the sequel.

The eigenfunctions of the rotational diffusion operator $\Psi^L_{MK}(\Omega) = \sqrt{\frac{2L+1}{8\pi^2}}\mathcal{D}^L_{MK}(\Omega)$, which satisfy the normalization condition $\int d\Omega \left(\Psi^L_{MK}(\Omega)\right)^* \Psi^{L'}_{M'K'}(\Omega) = \delta_{L,L'}\delta_{M,M'}\delta_{K,K'}$, may be used to generate an eigenfunction expansion of Z_{ij} in terms of the complete set $\{\Psi^{L'}_{M'K'}(\Omega)\}$. For the secular g tensor problem, it is known that $\mathcal{H}_1(\Omega)$ does not couple $M, K \neq 0$ to the starting vector term proportional to p_0 on the right hand side of Equations 6 and 9, and one may therefore set $M = K = 0$ in the expansion of Z_{ij}. Furthermore, $\mathcal{H}_1(\Omega)$ only couples even values of L to $L = 0$ in this problem, so one may restrict L to even values alone. For the present problem, the following expansions are useful

$$Z_{\pm\mp} \equiv {\sum_{L'=0}^{\infty}}' \Psi^{L'}_{00}C^{L'}_{\pm\mp} \quad (10)$$

$$Z_{++} - Z_{--} \equiv {\sum_{L'=0}^{\infty}}' \sqrt{2}\Psi^{L'}_{00}C^{L'}_{p}, \quad (11)$$

where the factor $\sqrt{2}$ in Equation 11 is for later convenience. In Equations 10 and 11, the prime on the summation sign indicates that the summation is over even, non-negative values of L. Inserting these expansions into Equations 6–9, multiplying from the left by $\Psi^L_{00}(\Omega) = \left(\Psi^L_{00}(\Omega)\right)^*$ and integrating over Ω, one obtains the following set of coupled equations for the $C^{L'}$ spin operator matrix elements

$$(i\Delta\omega + E_L)C^L_{-+} - i\omega_2[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C^{L'}_{-+} + i\sqrt{2}dC^L_p = idq\delta_{L,0} \tag{12}$$

$$E_L C^L_p + i\sqrt{2}d(C^L_{-+} - C^L_{+-}) = 0 \tag{13}$$

$$(-i\Delta\omega + E_L)C^L_{+-} + i\omega_2[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C^{L'}_{+-} - i\sqrt{2}dC^L_p = -idq\delta_{L,0}, \tag{14}$$

where the following identity has been used in Equations 12 and 14

$$\int d\Omega\, \Psi^L_{00}(\Omega)\mathcal{D}^2_{00}(\Omega)\Psi^{L'}_{00} = [L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2, \tag{15}$$

and $[L] = \sqrt{2L+1}$, $[L'] = \sqrt{2L'+1}$ in Equation 15. In addition, $E_L = -RL(L+1)$ is the eigenvalue of the isotropic rotational diffusion operator relevant for this problem, and R is the rotational diffusion rate. Finally, $\Delta\omega = \omega - \omega_0$ is the frequency offset from exact resonance. Equations 12–14 may be rewritten in matrix form $\mathbf{X}\cdot\mathbf{C} = \mathbf{V}$ where $\mathbf{C}$ is the column vector of density matrix transitions and $\mathbf{V}$ is the columnar starting vector, which has non-vanishing entries only for $L = 0$ in the absence of the stochastic spin torque terms discussed in Section 3. Note that $\mathbf{X}$ is a mapping of one transition $\{ij\}$ to another $\{i'j'\}$. For the secular g-tensor problem, $\mathbf{X}$ is block tridiagonal, and each block is a 3×3 complex symmetric matrix. In order to see this more clearly, one may consider two limiting cases. First, the Bloch equation limit, where the rotational diffusion is so rapid that only the averaged value of the electron Zeeman interaction, corresponding to ω_0 is observed. The second is the Redfield limit where only $L = 0$ and $L = 2$ terms are retained.

1.1 Bloch Equation Limit

When the tumbling is sufficiently rapid, only the $L = 0$ terms in Equations 12–14 need be retained. For Equations 12 and 14 one may modify E_L to account for an intrinsic linewidth as follows $E_L \rightarrow -RL(L+1) - 1/T_2$ where $1/T_2$ is the intrinsic linewidth. For Equation 13, there is also an intrinsic time constant for recovery to the equilibrium state, the spin-lattice relaxation time, modeled by $1/T_1$ or $2W_e$. In that case E_L for the population difference is modeled by $E_L \rightarrow -RL(L+1) - 1/T_1$. Note further that $\begin{pmatrix} 0 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix} = 0$, so there is no direct coupling to the anisotropy of the electron Zeeman interaction in the Bloch limit. For this case, the coupled equations of motion reduce to

$$\begin{bmatrix} i\Delta\omega - 1/T_2 & \sqrt{2}id & 0 \\ \sqrt{2}id & -1/T_1 & -\sqrt{2}id \\ 0 & -\sqrt{2}id & -i\Delta\omega - 1/T_2 \end{bmatrix}\begin{bmatrix} C^0_{-+} \\ C^0_p \\ C^0_{+-} \end{bmatrix} = idq\begin{bmatrix} 1 \\ 0 \\ -1 \end{bmatrix} \tag{16}$$

Careful inspection of Equation 16 reveals that C^0_{-+} and C^0_{+-} are complex conjugates of one another, which is a special case of a more general result[4]: $C^{(n)}_{ij} = (C^{(-n)}_{ji})^*$. Note that when comparing expressions given here to Freed and coworkers[4], a different normalization is used. Also, recall that the Floquet index is suppressed here, as it is encoded in the ij subscripts, and that the superscript in Equation 16 references the L value. The normalization used here is similar to more symmetric forms developed later[11, 10, 8, 9, 5, 6]. Equation 16 is also in the form $\mathbf{X} \cdot \mathbf{C} = \mathbf{V}$ and one may solve for C by matrix inversion. Due to the symmetric structure of Equation 16, this can even be done by hand without too much effort, which is a useful exercise. The solution for $\mathbf{C}$ is

$$\mathbf{C} \equiv \begin{bmatrix} C^0_{-+} \\ C^0_p \\ C^0_{+-} \end{bmatrix} = -\frac{T_1 T_2^2 (dq)}{1 + (\Delta\omega T_2)^2 + d^2 T_1 T_2} \begin{bmatrix} i\left(i\Delta\omega + \frac{1}{T_2}\right)/T_1 \\ -2\sqrt{2}d/T_2 \\ i\left(i\Delta\omega - \frac{1}{T_2}\right)/T_1 \end{bmatrix} \tag{17}$$

Equation 17 is an instance of the identity $C^{(n)}_{-+} = \left(C^{(-n)}_{+-}\right)^*$ introduced above. In order to project out the real and imaginary parts of C_{-+}, introduce the row vectors $\mathbf{C}' = [1 \quad 0 \quad 1]/2$ and $\mathbf{C}'' = [i \quad 0 \quad -i]/2$. Then, $C' \equiv \mathbf{C}' \cdot \mathbf{C}$ and $C'' \equiv \mathbf{C}'' \cdot \mathbf{C}$. Recall that $\sqrt{2}C_p$ is proportional to the population difference $Z_{++} - Z_{--}$. Thus, the row vector $\mathbf{C}_p = [0 \quad 1 \quad 0]/2\sqrt{2}$ projects out the population difference, and $C_0 \equiv \mathbf{C_p} \cdot \mathbf{C}$. Collecting the results, one finds

$$C' = \frac{(\Delta\omega T_2)(dqT_2)}{1 + (\Delta\omega)^2 T_2^2 + d^2 T_1 T_2} \tag{18}$$

$$C'' = \frac{(dqT_2)}{1 + (\Delta\omega)^2 T_2^2 + d^2 T_1 T_2} \tag{19}$$

$$C_0 = \frac{d^2 T_1 T_2 q}{1 + (\Delta\omega)^2 T_2^2 + d^2 T_1 T_2} \tag{20}$$

Equations 18–20 may be identified with the standard solutions of the saturated Bloch equations when it is recalled that C_0 is the deviation from the equilibrium magnetization, which is also proportional to q. Up to a normalization constant, therefore, Equations 18–20 may be rewritten in standard Bloch form in the rotating frame

$$\begin{aligned} M_x &= M_0 \frac{(\Delta\omega T_2)(dT_2)}{1 + (\Delta\omega)^2 T_2^2 + d^2 T_1 T_2} \\ M_y &= M_0 \frac{(dqT_2)}{1 + (\Delta\omega)^2 T_2^2 + d^2 T_1 T_2} \\ M_z &= M_0 \frac{1 + (\Delta\omega^2) T_1 T_2}{1 + (\Delta\omega)^2 T_2^2 + d^2 T_1 T_2} \end{aligned} \tag{21}$$

Redefining the starting vector $V^T \equiv i\sqrt{\frac{dq}{2}}[1 \quad 0 \quad -1]$, the desired experimental quantity, M_y in Equation 21 is seen to be proportional to $V^T \cdot X^{-1} \cdot V$. In bra/ket notation, this is equivalent to $\langle\, V \,|\, X^{-1} \,|\, V \,\rangle$, but the bra and ket are related by transposition, not hermitian conjugation. This same bra/ket inner product is required in the linear response lineshape calculation[10]. There, the norm of the starting vector is taken as unity. For the present problem, it is useful to use the dimensional norm $\langle\, V \,|\, V \,\rangle = -dq$, which is not positive definite.

1.2 Redfield Limit

The Redfield limit occurs when the rotational tumbling is sufficiently rapid that only the $L = 0$ and $L = 2$ terms need be retained. In that case, the matrix representation of the stochastic Liouville operator is a 6×6 matrix in block tri-diagonal form, where each block is a 3×3 matrix. A concise representation is possible if the following abbreviations are introduced

$$K_{LL'} = \Delta\omega\delta_{L,L'} - \omega_2[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2. \tag{22}$$

It is seen that $K_{LL'} = K_{L'L}$ in Equation 22 due to the symmetries of the Wigner 3j symbols. The quantity

$$R_L = RL(L+1) + 1/T_2 \tag{23}$$

models the rotational modulation of the $\pm\mp$ coherences. Equation 23 has an analogue for the rotational modulation of the population difference

$$W_L = RL(L+1) + 1/T_1. \tag{24}$$

In terms of Equations 22–24 the matrix representation of the SLE may be written compactly in the Redfield limit as follows

$$\begin{bmatrix} iK_{00} - R_0 & \sqrt{2}id & 0 & iK_{02} & 0 & 0 \\ \sqrt{2}id & -W_0 & -\sqrt{2}id & 0 & 0 & 0 \\ 0 & -\sqrt{2}id & -iK_{00} & 0 & 0 & -iK_{02} \\ iK_{20} & 0 & 0 & iK_{22} - R_2 & \sqrt{2}id & 0 \\ 0 & 0 & 0 & \sqrt{2}id & -W_2 & -\sqrt{2}id \\ 0 & 0 & -iK_{20} & 0 & -\sqrt{2}id & -iK_{22} - R_2 \end{bmatrix} \cdot \begin{bmatrix} C^0_{-+} \\ C^0_p \\ C^0_{+-} \\ C^2_{-+} \\ C^2_p \\ C^2_{+-} \end{bmatrix} = \begin{bmatrix} iqd \\ 0 \\ -iqd \\ 0 \\ 0 \\ 0 \end{bmatrix} \tag{25}$$

If it is only desired to observe the M_y component of the magnetization, then some simplifications may be applied to the coupled Equations 12–14. First note that within each block $L = L'$ Equation 13 may be used to eliminate C^0_p from Equations 14 and 12. Second, note that this transformation will not affect the 'off-diagonal' blocks $L' = L \pm 2$. This matrix partitioning will introduce a new quantity[8]

$$S_L = -2dW_L^{-1}d^T, \tag{26}$$

where the matrix transpose operation is introduced with an eye to future applications. When C^L_p is eliminated from the steady state equation of motion for $\mathbf{C}$, one finds in the Redfield limit

$$\begin{bmatrix} iK_{00} - R_0 + S_0 & -S_0 & iK_{02} & 0 \\ -S_0 & -iK_{00} - R_0 + S_0 & 0 & -iK_{02} \\ iK_{20} & 0 & iK_{22} - R_2 + S_2 & -S_2 \\ 0 & -iK_{20} & -S_2 & -iK_{22} - R_2 + S_2 \end{bmatrix} \cdot \begin{bmatrix} C^0_{-+} \\ C^0_{+-} \\ C^2_{-+} \\ C^2_{+-} \end{bmatrix} = \begin{bmatrix} iqd \\ -iqd \\ 0 \\ 0 \end{bmatrix}. \tag{27}$$

Written in this form, Equation 27 is still block tri-diagonal, but the matrix partitioning has reduced the size of the matrix and has removed the explicit dependence on quantities that are not directly observed experimentally in conventional EPR experiments. Equation 27 can be expressed in Risken's notation[12] as follows

$$\begin{bmatrix} \mathbf{Q}_0 & \mathbf{Q}_0^+ \\ \mathbf{Q}_2^- & \mathbf{Q}_2 \end{bmatrix} \cdot \begin{bmatrix} \mathbf{C}_0 \\ \mathbf{C}_2 \end{bmatrix} = \begin{bmatrix} \mathbf{V}_0 \\ \mathbf{V}_2 \end{bmatrix}, \tag{28}$$

where all quantities in Equation 28 are to be understood as 2×2 or 2×1 matrices depending on context. Note further that in this problem $\mathbf{Q}_0^+ = \mathbf{Q}_2^-$. Using the methods outlined in Risken's text[12, c. 9], one may compute

$$\mathbf{C}_0 = \left[\mathbf{Q}_0 - \mathbf{Q}_0^+ \left[\mathbf{Q}_2\right]^{-1} \mathbf{Q}_2^-\right]^{-1} \mathbf{V}_0, \tag{29}$$

where $\mathbf{V}_L = \mathbf{V}_0 \delta_{L,0}$ and $[\cdot]^{-1}$ refers to the matrix inverse of the quantity in square brackets. The M_y magnetization may be computed from

$$M_y(\Delta\omega) = \mathbf{V_0}^T \cdot \left[\mathbf{Q}_0 - \mathbf{Q}_0^+ \left[\mathbf{Q}_2\right]^{-1} \mathbf{Q}_2^-\right]^{-1} \mathbf{V}_0, \tag{30}$$

where the starting vector components in Equation 30 may be renormalized according to the discussion after Equation 21. For the present case, this implies $qd \rightarrow \sqrt{qd/2}$.

It is a straightforward but tedious exercise to explicitly evaluate Equation 30. Defining $\delta = K_{20}^2/[(R_2 - S_2)^2 + K_{22}^2 - S_2^2]$ one finds

$$M_y(\Delta\omega) = \frac{qd(R_0 + \delta R_2)}{(K_{00} - \delta K_{22})^2 + [(R_0 + \delta R_2) - (S_0 + \delta S_2)]^2 - (S_0 + \delta S_2)^2}. \tag{31}$$

Equation 31 is exact in the Redfield approximation. One may simplify Equation 31 by noting that δ is a small quantity. In particular

$$\delta = \frac{\omega_2^2/5}{(6R + 1/T_2 + 2d^2/(6R + 1/T_1))^2 + (\Delta\omega - \omega_2/\sqrt{5})^2 - (2d^2/(6R + 1/T_1))^2}, \tag{32}$$

where Equations 22–26 and the observation that $\begin{pmatrix} 2 & 2 & 0 \\ 0 & 0 & 0 \end{pmatrix} = 1/\sqrt{5}$ have been used to write the explicit form for Equation 32. When the Redfield approximation is valid, the following inequality typically obtains $R \gg 1/T_1, 1/T_2$. In addition, for moderate saturation, one may often, but not always, assume that $R \gg d$. When these inequalities are satisfied, one may approximate $\delta \approx (1/180)(\omega_2^2/R^2)$. The approximate expression for the lineshape then becomes

$$M_y/M_0 = \frac{1}{\pi} \frac{(1/T_2 + \delta\, 6R)}{(1/T_2 + \delta\, 6R)^2 + (\Delta\omega - \delta\, \omega_2/\sqrt{5})^2}. \tag{33}$$

Note that Equation 33 is a Lorentzian lineshape. According to recent published work[13], this means that Equation 33 may be interpreted as a probability density function (PDF). Physically, it is proportional to the photon absorption cross section. The factor of $1/\pi$ ensures that the integrated lineshape is normalized. The linewidth decreases as R increases and the resonant frequency has a dynamic frequency shift. These

are all features that are known for the non-saturated lineshape. As d inscreases, one may model the effect of saturation by using the full expression for M_y, Equation 31.

One may use these results to modify the Bloch limit solutions discussed in Section 1.1 by incorporating the dynamic frequency shift and diffusion rate dependent $1/T_2$ introduced here. The result is that Equation 21 can be modified to account for Redfield-type correction terms with the substitutions $\omega_0 \rightarrow \omega_0 + \delta\,\omega_2/\sqrt{5}$ and $1/T_2 \rightarrow 1/T_2 + \delta\,6R$.

2 Slow Tumbling Regime

When $|\omega_2/R| \ll 1$ the Redfield approximation breaks down, and one must consider higher order terms in Equation 28. In particular the structure of the coupled equations of motion for the partitioned matrix becomes

$$\begin{bmatrix} \mathbf{Q}_0 & \mathbf{Q}_0^+ & \mathbf{0} & & \dots & \mathbf{0} \\ \mathbf{Q}_2^- & \mathbf{Q}_2 & \mathbf{Q}_2^+ & \mathbf{0} & & \vdots \\ \mathbf{0} & \ddots & \ddots & \ddots & \ddots & \mathbf{0} \\ \vdots & & & \mathbf{Q}_{N-2}^- & \mathbf{Q}_{N-2} & \mathbf{Q}_{N-2}^+ \\ \mathbf{0} & \dots & & \mathbf{0} & \mathbf{Q}_N^- & \mathbf{Q}_N \end{bmatrix} \cdot \begin{bmatrix} \mathbf{C}_0 \\ \mathbf{C}_2 \\ \vdots \\ \mathbf{C}_{N-2} \\ \mathbf{C}_N \end{bmatrix} = \begin{bmatrix} \mathbf{V}_0 \\ \mathbf{V}_2 \\ \vdots \\ \mathbf{V}_{N-2} \\ \mathbf{V}_N \end{bmatrix}, \tag{34}$$

It is assumed that Equation 34 can be truncated at some finite N value. Note further that the symmetry $\left[\mathbf{Q}_{M+2}^-\right]^{\mathrm{T}} = \mathbf{Q}_M^+, 0 \le M \le N-2$ ensures that Equation 34 is a complex symmetric, block tri-diagonal matrix. The notation $[\cdot]^{\mathrm{T}}$ indicates the operation of taking the matrix transpose of the object in square brackets. Equation 34 also has the structure of a finite, three-term vector recurrence relation[12]. Thus an alternative expression for Equation 34 is

$$\begin{aligned} \mathbf{Q}_0^-\mathbf{C}_0 + \mathbf{Q}_0\mathbf{C}_2 &= \mathbf{V}_0 \\ \mathbf{Q}_2^-\mathbf{C}_0 + \mathbf{Q}_2\mathbf{C}_2 + \mathbf{Q}_2^+\mathbf{C}_4 &= \mathbf{0} \\ &\vdots \\ \mathbf{Q}_{N-2}^-\mathbf{C}_{N-4} + \mathbf{Q}_{N-2}\mathbf{C}_{N-2} + \mathbf{Q}_{N-2}^+\mathbf{C}_N &= \mathbf{0} \\ \mathbf{Q}_N^-\mathbf{C}_{N-2} + \mathbf{Q}_N\mathbf{C}_N &= \mathbf{0}. \end{aligned} \tag{35}$$

Starting with Equation 35, one may perform successive backsubstitutions to derive an explicit form for $\mathbf{C_0}$. The only complicating feature is that one must keep track of the order of the non-commuting $\mathbf{Q}$ matrices. When this is done, the answer may be shown to be[12]

$$\mathbf{C}_0 = \left[\mathbf{Q}_0 - \mathbf{Q}_0^+\left[\mathbf{Q}_2 - \mathbf{Q}_2^+\left[\mathbf{Q}_4 - \mathbf{Q}_4^+\left[\mathbf{Q}_6 \cdots\right]^{-1}\mathbf{Q}_6^-\right]^{-1}\mathbf{Q}_4^-\right]^{-1}\mathbf{Q}_2^-\right]^{-1}\mathbf{V}_0, \tag{36}$$

which has the form of a matrix continued fraction. Due to the matrix structure of Equation 36, the only way known to the author to evaluate the continued fraction is downward from N. Note that the problem comes

from the $\mathbf{Q}_M^-$ terms in Equation 36. From the structure of the system of Equations 36, one sees that the difficulties due to the $\mathbf{Q}_M^-$ terms can be removed by multiplying each equation in the system of Equations 36 by $\left[\mathbf{Q}_M^-\right]^{-1}$, where $\left[\mathbf{Q}_0^-\right]^{-1} \equiv \mathbf{1}_{2\times 2}$, the 2×2 identity matrix. Define renormalized $\mathbf{Q}$ matrices as follows $\mathbf{q}_N \equiv \left[\mathbf{Q}_N^-\right]^{-1} \mathbf{Q}_N$, $\mathbf{q}_N^+ \equiv \left[\mathbf{Q}_N^-\right]^{-1} \mathbf{Q}_N^+$. When this transformation is applied to the system of Equations 36, the resulting continued fraction may be written as follows

$$\mathbf{C}_0 = \left[\mathbf{q}_0 - \mathbf{q}_0^+ \left[\mathbf{q}_2 - \mathbf{q}_2^+ \left[\mathbf{q}_4 - \mathbf{q}_4^+ \left[\mathbf{q}_6 \cdots\right]^{-1}\right]^{-1}\right]^{-1}\right]^{-1} \mathbf{V}_0, \tag{37}$$

As Risken shows[12], Equation 37 is in a form suitable for evaluation by upward recurrence, as will be seen.

Given: two sequences $\mathbf{b}_{(M+2)/2} = \mathbf{q}_M$, where $\mathbf{b}_0 = 0$; and $\mathbf{a}_{(M+4)/2} = -\mathbf{q}_M^+$, where $\mathbf{a}_1 \equiv \mathbf{1}$; and both sequences are subject to the condition $M \geq 0$, then the following recurrence relations

$$\begin{aligned} \mathbf{A}_n &= \mathbf{A}_{n-1}\mathbf{b}_n + \mathbf{A}_{n-2}\mathbf{a}_n \\ \mathbf{B}_n &= \mathbf{B}_{n-1}\mathbf{b}_n + \mathbf{B}_{n-2}\mathbf{a}_n \end{aligned} \tag{38}$$

define the n^{th} approximant to $\mathbf{C}_0(n) \approx \mathbf{A}_n\mathbf{B}_n^{-1}$ subject to the initial conditions:

$$\begin{aligned} \mathbf{A}_{-1} &= \mathbf{1} \\ \mathbf{A}_0 &= \mathbf{b}_0 \\ \mathbf{B}_{-1} &= \mathbf{0} \\ \mathbf{B}_0 &= \mathbf{1}. \end{aligned}$$

The proof proceeds by induction. Consider the first order approximant $\mathbf{C}_0(1)$. Using the definitions introduced above, one finds

$$\begin{aligned} \mathbf{A}_1 = \mathbf{A}_0\mathbf{b}_1 + \mathbf{A}_{-1}\mathbf{a}_1 &= \mathbf{1} \\ \mathbf{B}_1 = \mathbf{B}_0\mathbf{b}_1 + \mathbf{B}_{-1}\mathbf{a}_1 &= \mathbf{q}_0, \end{aligned}$$

which implies $\mathbf{C}_0(1) = \mathbf{A}_1\mathbf{B}_1^{-1}$ and leads to $\mathbf{C}_0(1) = \mathbf{1}\mathbf{q}_0^{-1} = \mathbf{q}_0^{-1}$. This is the correct lowest order result, equivalent to computing the elements of the transverse magnetization in the Bloch limit. The second order approximant $\mathbf{C}_0(2)$ may be computed from

$$\begin{aligned} \mathbf{A}_2 = \mathbf{A}_1\mathbf{b}_2 + \mathbf{A}_0\mathbf{a}_2 &= \mathbf{q}_2 \\ \mathbf{B}_2 = \mathbf{B}_1\mathbf{b}_2 + \mathbf{B}_0\mathbf{a}_2 &= \mathbf{q}_0\mathbf{q}_2 - \mathbf{q}_0^+, \end{aligned}$$

leading to $\mathbf{C}_0(2) = \mathbf{A}_2\mathbf{B}_2^{-1} = \left[\mathbf{q}_0 - \mathbf{q}_0^+\mathbf{q}_2^{-1}\right]^{-1}$, which is the correct second order result, equivalent to the Redfield approximation. In order to derive this result, note the matrix identity $\mathbf{R}\mathbf{S}^{-1} = \left[\mathbf{S}\mathbf{R}^{-1}\right]^{-1}$ which allows one to simplify certain ratios of $\mathbf{q}$ matrices. Although one can verify the procedure for the next few values of n using the ratio identity introduced above, the manipulations rapidly grow tedious. A computer algebra system can eliminate most of the drudgery, however. Nevertheless, it is useful to have a proof valid

for any value of n. The cases $n = 1$ and $n = 2$ have been verified by direct calculation. Suppose the case $k = N/2$ is assumed to be true, that is,

$$\begin{aligned} \mathbf{A}_k &= \mathbf{A}_{k-1}\mathbf{b}_k + \mathbf{A}_{k-2}\mathbf{a}_k \\ \mathbf{B}_k &= \mathbf{B}_{k-1}\mathbf{b}_k + \mathbf{B}_{k-2}\mathbf{a}_k \\ \mathbf{C}_0(k) &= \mathbf{A}_k\mathbf{B}_k^{-1}. \end{aligned}$$

Note that the next case $k + 1 = (N/2) + 1$ is the terminating step in the sequence $0 \leq k \leq N/2 + 1$ as $\mathbf{b}_{(N/2)+1} = \mathbf{q}_N$, $\mathbf{a}_{(N/2)+1} = -\mathbf{q}_{N-2}^+$ and N is an even integer by construction. Identifying the last element of the sequence indexed by $0 \leq k \leq (N/2) + 1$ by $\mathbf{b}'_{k+1} = \mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}$, the $k + 1$ approximant can be written in terms of the k approximant, as there are now k elements in the sequence with the definition of $\mathbf{b}'_{k+1}$. Thus

$$\begin{aligned} \mathbf{C}_0(k+1) &= \mathbf{A}_k\mathbf{B}_k^{-1} \\ &= \left[\mathbf{A}_{k-1}(\mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}) + \mathbf{A}_{k-2}\mathbf{a}_k\right]\left[\mathbf{B}_{k-1}(\mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}) + \mathbf{B}_{k-2}\mathbf{a}_k\right]^{-1} \\ &= \left[\mathbf{A}_{k-1}(\mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}) + \mathbf{A}_{k-2}\mathbf{a}_k\right]\mathbf{b}_{k+1}\mathbf{b}_{k+1}^{-1}\left[\mathbf{B}_{k-1}(\mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}) + \mathbf{B}_{k-2}\mathbf{a}_k\right]^{-1}, \end{aligned}$$

where the identity operation $\mathbf{b}_{k+1}\mathbf{b}_{k+1}^{-1}$ has been sandwiched between the matrix ratio in the last line. Using the identity $\mathbf{R}^{-1}\mathbf{S}^{-1} = [\mathbf{SR}]^{-1}$ and the observation that matrix multiplication is associative and distributive, the expression for $\mathbf{C}_0(k)$ can be further simplified

$$\begin{aligned} \mathbf{C}_0(k+1) &= \left[\mathbf{A}_{k-1}(\mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}) + \mathbf{A}_{k-2}\mathbf{a}_k\right]\mathbf{b}_{k+1}\left[\left[\mathbf{B}_{k-1}(\mathbf{b}_k + \mathbf{a}_{k+1}\mathbf{b}_{k+1}^{-1}) + \mathbf{B}_{k-2}\mathbf{a}_k\right]\mathbf{b}_{k+1}\right]^{-1} \\ &= \left[\mathbf{A}_{k-1}(\mathbf{b}_k\mathbf{b}_{k+1} + \mathbf{a}_{k+1}) + \mathbf{A}_{k-2}\mathbf{a}_k\mathbf{b}_{k+1}\right]\left[\mathbf{B}_{k-1}(\mathbf{b}_k\mathbf{b}_{k+1} + \mathbf{a}_{k+1}) + \mathbf{B}_{k-2}\mathbf{a}_k\mathbf{b}_{k+1}\right]^{-1} \\ &= \left[(\mathbf{A}_{k-1}\mathbf{b}_k + \mathbf{A}_{k-2}\mathbf{a}_k)\mathbf{b}_{k+1} + \mathbf{A}_{k-1}\mathbf{a}_{k+1}\right]\left[(\mathbf{B}_{k-1}\mathbf{b}_k + \mathbf{B}_{k-2}\mathbf{a}_k)\mathbf{b}_{k+1} + \mathbf{B}_{k-1}\mathbf{a}_{k+1})\right]^{-1} \\ &= \left[\mathbf{A}_k\mathbf{b}_{k+1} + \mathbf{A}_{k-1}\mathbf{a}_{k+1}\right]\left[\mathbf{B}_k\mathbf{b}_{k+1} + \mathbf{B}_{k-1}\mathbf{a}_{k+1})\right]^{-1} \\ &= \mathbf{A}_{k+1}\mathbf{B}_{k+1}^{-1}, \quad \text{QED.} \end{aligned}$$

Note that this result for the scalar case is well-known[1], but the matrix case seems not to be written up explicitly anywhere. Risken[12], for example, states that the proof is by induction, but unless one sees the trick to writing it out in terms of the previous approximant in the sequence, the derivation is not straightforward. Given that a means of evaluating the recurrence upwards is now available, there is a well-defined procedure for evaluating the saturated secular g-tensor lineshape to any order in L iteratively. Explicit numerical examples will be given in Section 5. Further algorithms for systems of equations with block matrix form useful for spectral evaluation will also be given in Section 4. The author has found that, in his hands at least, the quickest numerical evaluation uses the built-in sparse array operations such as `\` and `/` in `octave`. It is useful to note, however, that exploration of the analytical properties of the solutions is facilitated by the availability of the matrix continued fraction representation. Explicit evaluation of the block

[1] Perhaps it was even known to Wallis in 1695.

matrix equations of motion are also facilitated by the existence of upward and downward matrix recurrences. These slower methods may also serve as useful checks on alternative methods of calculation.

3 Non-secular Contributions to the Lineshape

When saturation effects are important, then it is also important to consider the effect of non-secular contributions to the lineshape, as both kinds of contributions to the Hamiltonian are proportional to raising and lowering operators. The non-secular contributions to the Hamiltonian, in the notation of Schneider and Freed[9] can be expressed as follows

$$\begin{aligned} F_{\mathrm{g,M}}^{(2,0)} &= \sqrt{\frac{2}{3}}[g_{\parallel} - g_{\perp}] \left(\frac{\beta_e}{\hbar}\right) \\ A_{\mathrm{g,L}}^{(2,\pm 1)} &= \mp \frac{1}{2} B_0 S_{\pm} \\ \mathcal{H}_{\mathrm{non}}(\Omega) &= \sum_m \mathcal{D}^2_{m,0}(\Omega) F_{\mathrm{g,M}}^{(2,0)} A_{\mathrm{g,L}}^{2,m} \\ &= -\sqrt{\frac{3}{8}}\omega_2 \left[\mathcal{D}^2_{1,0} S_+ - \mathcal{D}^2_{-1,0} S_-\right]. \end{aligned} \tag{39}$$

Note that Equation 39 couples different M values in general through its dependence on $\mathcal{D}^2_{\pm 1,0}$. In the perturbative treatment given here, it will be seen that the explicit couplings to different M values can be eliminated. The M dependence of the non-secular terms is the reason for the breakdown of the M symmetrization introduced by Freed and coworkers[14, App. B] in non-perturbative treatments of the non-secular terms. Note that Meirovitch, *et al.*, has quite a few typos in Appendices A and B. Lee, *et al.*[5], is a more reliable source for accurate analytical expressions for matrix elements of the SLE.

Table 1 can be used to compute superoperator matrix elements of the non-secular terms with the Z coefficients and the equilibrium density matrix ρ_0. Note that unlike the saturation terms produced by $\mathcal{H}_2$, the non-secular terms in $\mathcal{H}_{\mathrm{non}}(\Omega)$ do not couple to different Floquet modes. One finds the following commutators for $-\frac{1}{i\hbar}\left[\mathcal{H}_{\mathrm{non}}(\Omega), Z^{(n)}\right]_{ij}$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\mathrm{non}}(\Omega), Z^{(n)}\right]_{++} = -i\sqrt{\frac{3}{8}}\omega_2 \left[\mathcal{D}^2_{1,0}(\Omega) Z^{(n)}_{-+} + \mathcal{D}^2_{-1,0}(\Omega) Z^{(n)}_{+-}\right] \tag{40}$$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\mathrm{non}}(\Omega), Z^{(n)}\right]_{+-} = -i\sqrt{\frac{3}{8}}\omega_2 \mathcal{D}^2_{1,0}(\Omega) \left[Z^{(n)}_{--} - Z^{(n)}_{++}\right] \tag{41}$$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\mathrm{non}}(\Omega), Z^{(n)}\right]_{-+} = i\sqrt{\frac{3}{8}}\omega_2 \mathcal{D}^2_{-1,0}(\Omega) \left[Z^{(n)}_{++} - Z^{(n)}_{--}\right] \tag{42}$$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\mathrm{non}}(\Omega), Z^{(n)}\right]_{--} = i\sqrt{\frac{3}{8}}\omega_2 \left[\mathcal{D}^2_{-1,0}(\Omega) Z^{(n)}_{+-} + \mathcal{D}^2_{1,0}(\Omega) Z^{(n)}_{-+}\right] \tag{43}$$

When non-secular terms are included in a calculation, Equations 40–43 may be added to the left hand sides of Equations 6–9 as appropriate. In addition, the starting vector terms arising from the $-\frac{1}{i\hbar}\left[\mathcal{H}(\Omega, t), \rho_0\right]$ commutator is modified in the presence of non-secular terms. One finds that Equations 6–9 are also augmented

by the following terms on their left hand sides

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\rm non}(\Omega),\rho_0\right]_{++} = 0 \quad (44)$$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\rm non}(\Omega),\rho_0\right]_{+-} = -i\sqrt{\frac{3}{8}}qp_0\sqrt{8\pi}\omega_2\mathcal{D}^2_{1,0}\delta_{n,0} \quad (45)$$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\rm non}(\Omega),\rho_0\right]_{-+} = -i\sqrt{\frac{3}{8}}qp_0\sqrt{8\pi}\omega_2\mathcal{D}^2_{-1,0}\delta_{n,0} \quad (46)$$

$$-\frac{1}{i\hbar}\left[\mathcal{H}_{\rm non}(\Omega),\rho_0\right]_{--} = 0 \quad (47)$$

Equations 44–47 are generally small in magnitude compared to the secular contributions to the starting vector, but such terms can be used to study the behavior of more complex spectral models, which have starting vectors that exhibit qualitatively similar behavior, *e.g.*, diffusion in a potential. Physically, the non-secular terms couple rotational eigenstates with various L and M values to the spin eigenstates. Thus, the term spin torque is appropriate[8]. In order to facilitate comparison to older literature on the subject, the definition $\omega_2 \equiv \mathcal{F}$ will sometimes be used.

Making the substitutions

$$\begin{aligned} Z^{(n)}_{\pm,\mp} &\equiv \sum_{L',K',M'} C^{(n)L'}_{\pm,\mp\, M',K'}\Psi^{L'}_{M',K'}(\Omega) \\ Z^{(n)}_{++} - Z^{(n)}_{--} &\equiv \sum_{L',K',M'} \sqrt{2}X^{(n)L'}_{M',K'}\Psi^{L'}_{M',K'}(\Omega) \end{aligned}$$

one may write down equations of motion for the $C^{(n)L'}_{\pm,\mp\, M',K'}$ and $X^{(n)L'}_{M',K'}$ states. Performing these substitutions, operating from the left with $\int d\Omega\, \left(\Psi^L_{M,K}(\Omega)\right)^*$, noting that $\left(\Psi^L_{M,K}(\Omega)\right)^* \equiv (-1)^{M-K}\Psi^L_{-M,-K}(\Omega)$ and observing that $\int d\Omega\, \Psi^L_{M,K}(\Omega)\mathcal{D}^{L'}_{M',K'}(\Omega)\Psi^{L''}_{M'',K''}(\Omega) \equiv [L][L']\begin{pmatrix} L & L' & L'' \\ M & M' & M'' \end{pmatrix}\begin{pmatrix} L & L' & L'' \\ K & K' & K'' \end{pmatrix}$, where $[L] \equiv \sqrt{2L+1}$, one obtains the following equation for the $X^{(n)L'}_{M',K'}$ state in the $n^{\rm th}$ Floquet mode

$$\begin{aligned} & (in\omega + \Gamma_{L,M,K})\sqrt{2}X^{(n)L}_{M,K} \\ -i\mathcal{F}\sqrt{\frac{3}{2}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}C^{(n)L'}_{-,+\, M',K'} & \\ -i\mathcal{F}\sqrt{\frac{3}{2}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & -1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}C^{(n)L'}_{+,-\, M',K'} & \\ +i2d\left[C^{(n-1)L}_{-,+\, M,K} - C^{(n-1)L}_{+,-\, M,K} + C^{(n+1)L}_{-,+\, M,K} - C^{(n+1)L}_{+,-\, M,K}\right] & \\ = 0, & \end{aligned}$$

where $\Gamma_{L,M,K}$ is the relaxation superoperator for the population difference, incorporating the intrinsic $1/T_1$. The equation of motion for the $C^{(n)}$ states depends on a related relaxation superoperator $\gamma_{L,M,K}$ which incorporates the intrinsic linewidth $1/T_2$. Note that in this case of a simple line, there are no cross relaxation terms, and thus no need to define the generalized (and usually singular) W matrix[11, 15]. It is seen that

the longitudinal coherence $X^{(n)L}_{M,K}$ is coupled not only to the $n \pm 1$ Floquet modes through the $C^{(n\pm1)L'}_{\pm,\mp\, M',K'}$ states coupled by the radiation field, but that there are also further couplings to $C^{(n)L}_{\pm,\mp\, M',K'}$ states through the non-secular contribution to the Hamiltonian. These additional terms will be treated perturbatively. In order to formulate a consistent perturbation theory, it is therefore necessary to have equations of motion for the $C^{(n)L}_{\pm,\mp\, M',K'}$ states. Following the same procedure as outlined above, one finds for $C^{(n)L}_{+,-\, M,K}$

$$\begin{aligned}
&(in\omega + i\omega_0 + \gamma_{L,M,K})C^{(n)L}_{+,-\,M,K} \\
&+i\mathcal{F}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 0 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}C^{(n)L'}_{+,-\,M',K'} \\
&+i\mathcal{F}\sqrt{\frac{3}{8}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}\sqrt{2}X^{(n)L'}_{M',K'} \\
&-id\sqrt{2}\left[X^{(n-1)L}_{M,K} + X^{(n+1)L}_{M,K}\right] \\
&-i\mathcal{F}\sqrt{\frac{3}{8}}q\,\delta_{n,0}\delta_{K,0}\delta_{M,1} \\
&= \quad -idq\left(\delta_{n,1} + \delta_{n,-1}\right).
\end{aligned}$$

Similarly, the equation for $C^{(n)L}_{-,+\, M,K}$ becomes

$$\begin{aligned}
&(in\omega - i\omega_0 + \gamma_{L,M,K})C^{(n)L}_{-,+\,M,K} \\
&-i\mathcal{F}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 0 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}C^{(n)L'}_{-,+\,M',K'} \\
&+i\mathcal{F}\sqrt{\frac{3}{8}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & -1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}\sqrt{2}X^{(n)L'}_{M',K'} \\
&+id\sqrt{2}\left[X^{(n-1)L}_{M,K} + X^{(n+1)L}_{M,K}\right] \\
&-i\mathcal{F}\sqrt{\frac{3}{8}}q\,\delta_{n,0}\delta_{K,0}\delta_{M,-1} \\
&= \quad idq\left(\delta_{n,1} + \delta_{n,-1}\right).
\end{aligned}$$

In these equations, one may identify the quantities with the largest magnitudes by analogy to the secular (or axial) approximation: $C^{(1)L}_{-,+\,M,K}$, $X^{(0)L}_{M,K}$ and $C^{(-1)L}_{+,-\,M,K}$. These terms arise from the $n \in \{-1, 0, 1\}$ Floquet modes. In the moderate saturation approximation, one may drop couplings to the $n = \pm 2$ Floquet modes as they will only make a small contribution. The criterion for identifying significant quantities is to examine the coefficient of the first term in the coupled equations of motion. If the coefficient depends on the sweep variable $\omega - \omega_0$ as is the case for the $n = \pm 1$ Floquet modes, or is independent of ω and ω_0, as is the case for $X^{(0)L}_{M,K}$, then the coefficient is small compared to others in the equations of motion and those terms should be retained. The remaining candidate terms would essentially oscillate at ω_0 or multiples of ω_0 and may be dropped in the RWA and high field approximations. In particular, the following terms are necessarily small by this criterion: $C^{(1)L}_{+,-\,M,K}$, $C^{(-1)L}_{-,+\,M,K}$, $C^{(0)L}_{+,-\,M,K}$, $C^{(0)L}_{-,+\,M,K}$, $X^{(1)L}_{M,K}$ and $X^{(-1)L}_{M,K}$. For the case of multi-

quantum EPR, where two excitation fields are used, one would need to reevaluate this criterion in terms of sum and difference frequencies of various harmonics[16]. Retaining only the terms $n \in \{-1, 0, 1\}$ in the coupled equations of motion, there are thus nine coupled matrix equations in nine unknown transition state vectors, subject to the state vector of 'initial conditions', the terms proportional to qd.

Upon identifying the most important couplings, one finds the following equations for $C^{(1)L}_{-,+\,M,K}$ and $X^{(1)L}_{M,K}$

$$\begin{aligned}
&(i(\omega-\omega_0)+\gamma_{L,M,K})C^{(1)L}_{-,+\,M,K} \\
&-i\mathcal{F}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 0 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}C^{(1)L'}_{-,+\,M',K'} \\
&+i\mathcal{F}\sqrt{\frac{3}{8}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & -1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}\sqrt{2}X^{(1)L'}_{M',K'} \\
&+id\sqrt{2}\left[X^{(0)L}_{M,K}\right] = idq, \\
&\frac{i\mathcal{F}}{i\omega+\Gamma_{L',M',K'}}(-1)^{M'-K'}\sqrt{\frac{3}{2}}\sum_{L'',M'',K''}[L'][L'']\begin{pmatrix} L' & 2 & L'' \\ -M' & 1 & M'' \end{pmatrix}\begin{pmatrix} L' & 2 & L'' \\ -K' & 0 & K'' \end{pmatrix}C^{(1)L''}_{-,+\,M'',K''} \\
&= \sqrt{2}X^{(1)L'}_{M',K'}.
\end{aligned}$$

One may use the second equation to eliminate $X^{(1)L'}_{M',K'}$ from the first. Note that this perturbative treatment of $X^{(1)L'}_{M',K'}$ will lead to a dynamic frequency shift and a non-secular contribution to the linewidth. These terms have been dropped previously[4], but retaining them does not lead to further difficulties. One may write down a similar set of equations for the coupled $C^{(-1)L}_{+,-\,M',K'}$ and $X^{(-1)L'}_{M',K'}$ states:

$$\begin{aligned}
&(-i(\omega-\omega_0)+\gamma_{L,M,K})C^{(-1)L}_{+,-\,M,K} \\
&+i\mathcal{F}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 0 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}C^{(-1)L'}_{+,-\,M',K'} \\
&+i\mathcal{F}\sqrt{\frac{3}{8}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L \\ -K & 0 & K' \end{pmatrix}\sqrt{2}X^{(-1)L'}_{M',K'} \\
&-id\sqrt{2}\left[X^{(0)L}_{M,K}\right] = -idq, \\
&\frac{i\mathcal{F}}{-i\omega+\Gamma_{L',M',K'}}(-1)^{M'-K'}\sqrt{\frac{3}{2}}\sum_{L'',M'',K''}[L'][L'']\begin{pmatrix} L' & 2 & L'' \\ -M' & -1 & M'' \end{pmatrix}\begin{pmatrix} L' & 2 & L'' \\ -K' & 0 & K'' \end{pmatrix}C^{(1)L''}_{+,-\,M'',K''} \\
&= \sqrt{2}X^{(-1)L'}_{M',K'},
\end{aligned}$$

which may be handled similarly to the equation for $C^{(1)L}_{-,+\,M,K}$.

The relevant equation for the $n = 0$ Floquet mode is

$$\begin{aligned}
& & & & & & & & & \Gamma_{L,M,K}\sqrt{2}X^{(0)L}_{M,K} \\
& -i\mathcal{F}\sqrt{\frac{3}{2}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & 1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -K & 0 & K' \end{pmatrix}C^{(0)L'}_{-,+\,M',K'} & & & & & & & & \\
& -i\mathcal{F}\sqrt{\frac{3}{2}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -M & -1 & M' \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -K & 0 & K' \end{pmatrix}C^{(0)L'}_{+,1\,M',K'} & & & & & & & & \\
& & & & & & & & & +i2d\left[C^{(1)L}_{-,+\,M,K} - C^{(-1)L}_{+,-\,M,K}\right] \\
& & & & & & & & & +i2d\left[C^{(-1)L}_{-,+\,M,K} - C^{(1)L}_{+,-\,M,K}\right] & = & 0.
\end{aligned}$$

For the $n = 0$ Floquet mode, there are four subsidiary perturbation equations to consider for the quantities $C^{(0)L'}_{-,+\,M',K'}$, $C^{(0)L'}_{+,-\,M',K'}$, $C^{(-1)L'}_{-,+\,M',K'}$ and $C^{(1)L'}_{+,-\,M',K'}$. These quantities may all be expressed in terms of $X^{(0)L'}_{M',K'}$ in the approximations used here. One finds for the $n = 0$ correction terms:

$$\begin{aligned}
& C^{(0)L'}_{-,+\,M',K'} = \\
& \quad -\frac{i\mathcal{F}}{i\omega_0 + \gamma_{L',M',K'}}(-1)^{M'-K'}\sum_{L'',M'',K''}[L'][L'']\begin{pmatrix} L' & 2 & L'' \\ -M' & -1 & M'' \end{pmatrix}\begin{pmatrix} L' & 2 & L'' \\ -K' & 0 & K'' \end{pmatrix}\sqrt{2}X^{(0)L''}_{M'',K''} \\
& \quad +\frac{i\mathcal{F}}{-i\omega_0 + \gamma_{L',M',K'}}q\,\delta_{M',-1}\delta_{K',0} \\
& C^{(0)L'}_{+,-\,M',K'} = \\
& \quad -\frac{i\mathcal{F}}{i\omega_0 + \gamma_{L',M',K'}}(-1)^{M'-K'}\sum_{L'',M'',K''}[L'][L'']\begin{pmatrix} L' & 2 & L'' \\ -M' & 1 & M'' \end{pmatrix}\begin{pmatrix} L' & 2 & L'' \\ -K' & 0 & K'' \end{pmatrix}\sqrt{2}X^{(0)L''}_{M'',K''} \\
& \quad +\frac{i\mathcal{F}}{i\omega_0 + \gamma_{L',M',K'}}q\,\delta_{M',1}\delta_{K',0}.
\end{aligned}$$

The $n = \pm 1$ correction terms are

$$\begin{aligned}
C^{(-1)L}_{-,+\,M,K} &= -\frac{id}{-i(\omega+\omega_0) + \gamma_{L,M,K}}\sqrt{2}X^{(0)L}_{M,K} \\
C^{(1)L}_{+,-\,M,K} &= +\frac{id}{i(\omega+\omega_0) + \gamma_{L,M,K}}\sqrt{2}X^{(0)L}_{M,K}.
\end{aligned}$$

These last two equations may be combined to yield

$$i2d\left[C^{(-1)L}_{-,+\,M,K} - C^{(1)L}_{+,-\,M,K}\right] = 4d^2\frac{\gamma_{L,M,K}}{(\omega+\omega_0)^2 + (\gamma_{L,M,K})^2}\sqrt{2}X^{(0)L}_{M,K}.$$

In the high field approximation, $\omega - \omega_0 \ll \omega_0$. When this is so, the previous equation may be further simplified

$$i2d\left[C^{(-1)L}_{-,+\,M,K} - C^{(1)L}_{+,-\,M,K}\right] \approx d^2\frac{\gamma_{L,M,K}}{(\omega_0)^2 + (\gamma_{L,M,K}/2)^2}\sqrt{2}X^{(0)L}_{M,K}.$$

Similar considerations allow one to evaluate

$$
\begin{aligned}
&-i\mathcal{F}\sqrt{\frac{3}{2}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -M & 1 & M' \end{pmatrix}C^{(0)L'}_{-,+\,M',K'} \\
&-i\mathcal{F}\sqrt{\frac{3}{2}}(-1)^{M-K}\sum_{L',M',K'}[L][L']\begin{pmatrix} L & 2 & L' \\ -K & 0 & K \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ -M & -1 & M' \end{pmatrix}C^{(0)L'}_{+,-\,M',K'} \\
\approx\ & \frac{3}{2}\mathcal{F}^2\sum_{L',L''}[L][L']^2[L'']\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} L' & 2 & L'' \\ 1 & -1 & 0 \end{pmatrix}\frac{\gamma_{L',0,0}}{\omega_0^2+(\gamma_{L',0,0})^2}\sqrt{2}X^{(0)L''}_{0,0} \\
&+\frac{3}{2}\mathcal{F}^2q\sum_{L'}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix}\frac{\gamma_{L',0,0}}{\omega_0^2+(\gamma_{L',0,0})^2}
\end{aligned}
$$

The first term on the right hand side of this equation is the contribution of the non-secular term to $1/T_1$. The second term on the right hand side modifies the starting vector. It is smaller than the non-perturbed starting vector elements by a factor of $(\mathcal{F}/\omega_0)^2$. Note that there is an explicit assumption that the perturbation approximation only affects the original terms of the unperturbed matrix, and does not mix in new values of M. Given that K is also zero for cases of axial symmetry under the assumption that the magnetic and diffusion axes are coincident, one finds that the only relevant quantum number is again L. Furthermore, the lowest order perturbations are assumed to couple $L \leftrightarrow L' = L \pm 2 \leftrightarrow L'' = L$. Thus, all of the relevant terms are seen to correspond to either dynamic frequency shifts or linewidth contributions due to the non-secular terms in the Hamiltonian. All of these interlocking approximations lead to a tridiagonal matrix that still has the same structure as in the secular g-tensor problem. Only the details of the L dependence of the various terms differ. Applying these considerations to the perturbed equations for $C^{(1)L}_{-,+\,0,0}$ and $C^{(-1)L}_{+,-\,0,0}$ one finds

$$
\begin{aligned}
&[i\Delta\omega+\gamma_L]C^{(1)L}_{-,+\,0,0} \\
&-i\mathcal{F}\sum_{L'}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C^{(1)L'}_{-,+\,0,0} \\
&+\frac{3}{4}\sum_{L'}\frac{\mathcal{F}^2}{\omega_0^2+(\Gamma_{L'})^2}(-i\omega_0+\Gamma_{L'})[L]^2[L']^2\begin{pmatrix} L & 2 & L' \\ 0 & -1 & 1 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} L' & 2 & L \\ -1 & 1 & 0 \end{pmatrix}C^{(1)L}_{-,+\,0,0} \\
&+id\sqrt{2}X^{(0)L}_{0,0} = idq,
\end{aligned}
\tag{48}
$$

and

$$
\begin{aligned}
&[-i\Delta\omega+\gamma_L]C^{(-1)L}_{+,-\,0,0} \\
&+i\mathcal{F}\sum_{L'}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2 C^{(-1)L'}_{+,-\,0,0} \\
&+\frac{3}{4}\sum_{L'}\frac{\mathcal{F}^2}{\omega_0^2+(\Gamma_{L'})^2}(i\omega_0+\Gamma_{L'})[L]^2[L']^2\begin{pmatrix} L & 2 & L' \\ 0 & -1 & 1 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}^2\begin{pmatrix} L' & 2 & L \\ -1 & 1 & 0 \end{pmatrix}C^{(-1)L}_{+,-\,0,0} \\
&-id\sqrt{2}X^{(0)L}_{0,0} = -idq.
\end{aligned}
\tag{49}
$$

The perturbed equation for $X_{0,0}^{(0)L}$ reads

$$\begin{aligned}
&\Gamma_L\sqrt{2}X_{0,0}^{(0)L}\\
&+\frac{3}{2}\sum_{L'}\frac{\mathcal{F}^2}{\omega_0^2+(\gamma_{L'})^2}\gamma_{L'}[L]^2[L']^2\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1\end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix} L' & 2 & L \\ -1 & 1 & 0\end{pmatrix}\sqrt{2}X_{0,0}^{(0)L}\\
&+d^2\frac{\gamma_L}{\omega_0^2+(\gamma_L/2)^2}\sqrt{2}X_{0,0}^{(0)L}\\
&+i2d\left[C_{-,+\,0,0}^{(1)L}-C_{+,-\,0,0}^{(-1)L}\right]\\
=\;&-\frac{3}{2}q\sum_{L'}\frac{\mathcal{F}^2}{\omega_0^2+(\gamma_{L'})^2}\gamma_{L'}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1\end{pmatrix}
\end{aligned}\tag{50}$$

In Equations 48–50, the terms in blue are due to the non-secular perturbations. Note also that these perturbed equations are of the same form as Equations 12–14 and so the same trick of replacing $X_{0,0}^{(0)L}$ with $\left[C_{-,+\,0,0}^{(1)L}-C_{+,-\,0,0}^{(-1)L}\right]$, effectively partitioning the matrix, will work as before.

Eliminating $X_{0,0}^{(0)L}$ leads to the following equations of motion for $C_{-,+\,0,0}^{(1)L}$:

$$\begin{aligned}
&[i\Delta\omega+\gamma_L]C_{-,+\,0,0}^{(1)L}\\
&-i\mathcal{F}\sum_{L'}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}^2 C_{-,+\,0,0}^{(1)L'}\\
&+\frac{3}{4}\sum_{L'}\frac{\mathcal{F}^2}{\omega_0^2+(\Gamma_{L'})^2}(-i\omega_0+\Gamma_{L'})[L]^2[L']^2\begin{pmatrix} L & 2 & L' \\ 0 & -1 & 1\end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix} L' & 2 & L \\ -1 & 1 & 0\end{pmatrix}C_{-,+\,0,0}^{(1)L}\\
&+\frac{2d^2}{\Gamma'_L}\left[C_{-,+\,0,0}^{(1)L}-C_{+,-\,0,0}^{(-1)L}\right]\\
=\;&i(dq\,\delta_{L,0}+\frac{3}{2}dq'_L),
\end{aligned}\tag{51}$$

and $C_{+,-\,0,0}^{(-1)L}$:

$$\begin{aligned}
&[-i\Delta\omega+\gamma_L]C_{+,-\,0,0}^{(-1)L}\\
&+i\mathcal{F}\sum_{L'}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}^2 C_{+,-\,0,0}^{(-1)L'}\\
&+\frac{3}{4}\sum_{L'}\frac{\mathcal{F}^2}{\omega_0^2+(\Gamma_{L'})^2}(i\omega_0+\Gamma_{L'})[L]^2[L']^2\begin{pmatrix} L & 2 & L' \\ 0 & -1 & 1\end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix} L' & 2 & L \\ -1 & 1 & 0\end{pmatrix}C_{+,-\,0,0}^{(-1)L}\\
&-\frac{2d^2}{\Gamma'_L}\left[C_{-,+\,0,0}^{(1)L}-C_{+,-\,0,0}^{(-1)L}\right]\\
=\;&-i(dq\,\delta_{L,0}+\frac{3}{2}dq'_L).
\end{aligned}\tag{52}$$

In Equations 51 and 52 the following abbreviations have been introduced

$$\Gamma'_L=\Gamma_L+\frac{3}{2}\mathcal{F}^2\sum_{L'}\frac{\gamma_{L'}}{\omega_0^2+(\gamma_{L'})^2}[L]^2[L']^2\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1\end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0\end{pmatrix}^2\begin{pmatrix} L' & 2 & L \\ 1 & -1 & 0\end{pmatrix}+d^2\frac{\gamma_L}{\omega_0^2+(\gamma_L/2)^2},$$

and

$$q'_L = q\frac{1}{\Gamma'_L}\mathcal{F}^2\sum_{L'}\frac{\gamma_{L'}}{\omega_0^2+(\gamma_{L'})^2}[L][L']\begin{pmatrix} L & 2 & L' \\ 0 & 0 & 0 \end{pmatrix}\begin{pmatrix} L & 2 & L' \\ 0 & 1 & -1 \end{pmatrix}.$$

Note the second term on the right hand side of the expression for Γ'_L reduces to the expression for $W_e^{(G)}$ given in Freed and coworkers[4, Eq. 61] even though the perturbation expression for the non-secular contribution to the $1/T_1$ process derived here is different. Note that the third term on the right hand side is not given in the published perturbation calculation[4]. Physically, it arises from power broadening of the energy level lifetimes, coupled by the off-diagonal coherences $C^{(\pm1)L}_{\mp,\pm\,0,0}$. For a consistent treatment of non-secular contributions, both terms should be included. One finds, as in Freed and coworkers[4] that only the $L = 0$ term is signficantly affected

$$\Gamma'_0 = \frac{1}{T_1} + \frac{9}{5}\left(\frac{\mathcal{F}}{\omega_0}\right)^2 R + \left(\frac{d}{\omega_0}\right)^2\frac{1}{T_2} \tag{53}$$

Equation 53 generalizes the published result[4]. For $L \neq 0$, Γ'_L may be taken to be equal to Γ_L as the perturbations will be smaller by a factor of $(\mathcal{F}/\omega_0)^2$ or $(d/\omega_0)^2$ compared to $RL(L+1)$ assuming that $1/T_1$, $1/T_2$ and R do not differ too drastically in order of magnitude.

The treatment of the perturbation correction to the starting vector is different, however. There, the perturbation is roughly constant for $RL(L+1) \ll \omega_0$ and decays as $[RL(L+1)]^{-2}$ for $RL(L+1) \gg \omega_0$. Due to the diagonal dominance of rotational diffusion contributions to the SLE, one expects that the modified starting vector would have small effects. For non-Brownian diffusion, however, it is possible that the starting vector corrections for moderate L could have an appreciable effect on the lineshape, as the diffusion superoperator matrix elements increase more slowly for free or jump diffusion compared to Brownian diffusion[9, 8]. These assertions should be checked by spectral simulation.

4 Analytic Derivatives of the Saturated Axial g-Tensor Lineshape

In order to compute the sensitivity of the spectrum to the parameters, it is useful to compute spectral parameter derivatives[17]. As has been shown in Section 1, the spectrum may be represented symbolically as follows

$$I(\Delta\omega) = \langle\, v(d) \mid X(d, \Delta\omega, \omega_2, R)^{-1} \mid v(d)\,\rangle. \tag{54}$$

Starting from the identity $XX^{-1} = 1$ it is straightforward[17] to show that

$$\frac{\partial}{\partial\xi}X^{-1} = -X^{-1}\left(\frac{\partial}{\partial\xi}X\right)X^{-1} \tag{55}$$

Equation 55 is the matrix generalization of the familiar calculus identity $du^{-1}/dx = -u^{-2}du/dx$. If the starting vector $\mid v\,\rangle$ is independent of ξ then

$$\frac{\partial}{\partial\xi}I(\Delta\omega) = -\langle\, v \mid X^{-1}\left(\tfrac{\partial}{\partial\xi}X\right)X^{-1} \mid v\,\rangle. \tag{56}$$

Equation 56 is valid for the following parameters in the saturated lineshape problem: $\{\Delta\omega, R, 1/T_2, 1/T_1\}$ even when the non-secular correcions to the starting vector are included. If non-secular terms are not included then $\omega_2 = \mathcal{F}$ is also in this set. The strength of the transition moment $d = \omega_1/2$ appears in the starting vector, so quantifiers of the spectral sensitivity must take this dependence into account. Note that a symmetrized form of the starting vector is used here, proportional to $\sqrt{dq}$, so that

$$|\, v' \,\rangle \equiv \frac{\partial}{\partial d}|\, v \,\rangle = \frac{1}{2d}|\, v \,\rangle \tag{57}$$

Inserting Equation 57 into Equation 56 one finds

$$\frac{\partial}{\partial d} I(\Delta\omega) = \frac{1}{d}\langle\, v \mid X^{-1} \mid v \,\rangle - \langle\, v \mid X^{-1} \left(\tfrac{\partial}{\partial d} X\right) X^{-1} \mid v \,\rangle. \tag{58}$$

Using the definition of the spectrum, Equation 54, one may simplify Equation 58 further

$$\frac{\partial}{\partial d} I(\Delta\omega) = \frac{1}{d} I(\Delta\omega) - \langle\, v \mid X^{-1} \left(\tfrac{\partial}{\partial d} X\right) X^{-1} \mid v \,\rangle. \tag{59}$$

Note that this form for the derivative is valid even in the presence of the non-secular terms if terms of order $d^2/\omega_0^2 \ll 1$ in Γ'_L in the starting vector correction q'_L are dropped.

In general, the matrix X in Equation 59 is sparse, but not all of its elements depend on d, so $\partial X/\partial d$ is even more sparse than X. In addition, X is complex symmetric, so X^{-1} must be complex symmetric as well. This implies that $\left(X^{-1}\right)^T = X^{-1}$, where $(\cdot)^T$ is the matrix transpose operation applied to any operator between the parentheses. Given that bras and kets are related by $\langle\, v \mid = (|\, v \,\rangle)^T$ in this formalism, one has $\langle\, v \,| X^{-1} = \left(X^{-1}|\, v \,\rangle\right)^T$. Unlike the situation in Section 2, where one could just work with the continued fraction representation of $\mathbf{C}_0$, one needs access to all of the matrix elements of $X^{-1}|\, v \,\rangle$ due to the presence of $\partial X/\partial d$ in the final term of Equation 59. Finding the solution vector $X^{-1}|\, v \,\rangle$ is a standard problem in linear algebra, however. Numerical methods for computing the required inverses should exploit the tridiagonal structure. For tridiagonal matrices with scalar matrix elements, Golub and van Loan[17] give standard algorithms for finding solution vectors to $\mathbf{A} \cdot \mathbf{x} = \mathbf{b}$. For tridiagonal matrices with matrix entries, one must take care of the order of matrix operations. For this case one may decompose $X \equiv A = LD(M)^T$ where L and M are lower triangular matrices and D is a diagonal matrix[17]. For a block tridiagonal matrix, L and M each have only one (matrix) subdiagonal. The structure of these matrices is as follows

$$L = \begin{bmatrix} 1 & & & & \\ e_1 & 1 & & & \\ 0 & e_2 & 1 & & \\ & 0 & e_3 & 1 & \\ & & \ddots & \ddots & \ddots \end{bmatrix}, (M)^T = \begin{bmatrix} 1 & f_1 & & & \\ 0 & 1 & f_2 & & \\ & 0 & 1 & f_3 & \\ & & \ddots & \ddots & \ddots \end{bmatrix}$$

$$D = \begin{bmatrix} d_1 & 0 & & & \\ 0 & d_2 & 0 & & \\ & 0 & d_3 & 0 & \\ & & \ddots & \ddots & \ddots \end{bmatrix}$$

The block tridiagonal matrix A in this representation has the following explicit form

$$
\begin{aligned}
A &= LD(M)^T \\
\begin{bmatrix} a_{11} & a_{12} & & & \\ a_{21} & a_{22} & a_{23} & & \\ & a_{32} & a_{33} & a_{34} & \\ & & \ddots & \ddots & \ddots \end{bmatrix} &= \begin{bmatrix} 1 & & & & \\ e_1 & 1 & & & \\ 0 & e_2 & 1 & & \\ & 0 & e_3 & 1 & \\ & & \ddots & \ddots & \ddots \end{bmatrix} \cdot \\
&\cdot \begin{bmatrix} d_1 & 0 & & & \\ 0 & d_2 & 0 & & \\ & 0 & d_3 & 0 & \\ & & \ddots & \ddots & \ddots \end{bmatrix} \cdot \begin{bmatrix} 1 & f_1 & & & \\ 0 & 1 & f_2 & & \\ & 0 & 1 & f_3 & \\ & & \ddots & \ddots & \ddots \end{bmatrix} \\
&= \begin{bmatrix} d_1 & d_1 f_1 & & & \\ e_1 d_1 & d_2 + e_1 d_1 f_1 & d_2 f_2 & & \\ & e_2 d_2 & d_3 + e_2 d_2 f_2 & d_3 f_3 & \\ & & \ddots & \ddots & \ddots \end{bmatrix}
\end{aligned} \tag{60}
$$

The only complication in working with Equation 60 comes from keeping track of the explicit order of matrix operations. Recall that all 'matrix elements' in this case are 2×2 matrices. The matrix elements of L, D and M may be found by an iterative procedure. Once the matrix elements of L, D and M are known, the solution vector $x = A^{-1}b$ may be found by solving the following three (trivial) linear algebra problems[17]: $Ly = b$, which may be solved by forward substitution; $Dz = y$, which may be found by premultiplying y_k by $(d_k)^{-1}$; and $(M)^T x = z$, which may be solved by back substitution. The algorithm for finding the matrix elements of L, D and M is given below:

$$
\begin{aligned}
&\mathrm{k} = 1: \\
d_1 &= a_{1,1} \\
f_1 &= (d_1)^{-1} a_{1,2} \\
e_1 &= a_{2,1} (d_1)^{-1} \\
&\mathrm{k} > 1: \\
d_k &= a_{k,k} - a_{k,k-1} (d_{k-1})^{-1} a_{k-1,k} \\
f_k &= (d_k)^{-1} a_{k,k+1} \\
e_k &= a_{k+1,k} (d_k)^{-1}
\end{aligned}
$$

Note that this procedure may also be applied to non-symmetric block tri-diagonal matrices. The only requirement is that the diagonal block d_k be invertible. Including an intrinsic linewidth $1/T_2$ ensures this. Given the decomposition $A = LD(M)^T$ and a vector b, the following pseudocode implements the algorithm

that returns the solution to $Ax = b$, overwriting b in the process

```
t0 = b(1)
for k = 1:n-1
   t1 = b(k+1)-e(k).t0
   t0 = b(k+1)
   b(k+1) = t1
end
b = d.\b
t0 = b(n)
for k = n:-1:2
   t1 = b(k-1)-f(k-1).t0
   t0 = b(k-1)
   b(k-1) = t1
end
```

Here, `.` indicates matrix multiply and `.\` indicates element-wise 'left' division, where each 'element' in this case is a matrix. This algorithm is similar to the one discussed in Golub and van Loan[17, §4.5], which uses an LU decomposition instead of the $LD(M)^T$ decomposition used here.

5 Numerical Examples

Real soon now.

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