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Analytical approximations to inhomogeneously broadened, radiation damped free precession and echo signals

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ABSTRACT

The Dirac–Frenkel–Maclachlan (DFM) variation of parameters approach to approximately solving the time dependent Schrödinger equation is used to generate free precession and echo signals from the Bloch equations corrected for the effects of radiation damping and inhomogeneous broadening. Following a brief description of how the DFM method can be applied to the non-linear Bloch equations, two figures of merit designed to evaluate how a DFM optimized approximation compares with the exact solution is provided. This framework is used to optimize and evaluate the performance of six trial functions describing inhomogeneously broadened, radiation damped free precession and echo signals. The trial functions are then used to analyze the resolution enhancement and signal attenuation produced by pulse sequences that suppress radiation damping.

1. Introduction

Radiation damping, or the interaction of a freely precessing magnetization with itself mediated by coupling to the detection circuit, is well known in high resolution nuclear magnetic resonance (NMR) spectroscopy [1–5]. This effect is often considered a nuisance as the symptoms of radiation damping include line broadening in high field, high resolution spectra, radio frequency (rf) tank circuit tuning dependent spectral artifacts, and anomalous values for relaxation time constants [6–13]. The success of both active [14] and passive [15] methods for the suppression of radiation damping effects on free precession signals and their corresponding spectra relies on the fact that analytical solutions to the non-linear Bloch equations are available. Given the large body of work in the NMR community in connection with radiation damping since Suryan's initial work in 1949 [16], it is ironic that transient analytical solutions to the non-linear Bloch equations are still only available for just three cases. These analytical solutions correspond to a single precessing, radiation damped isochromat, which is either alone [3,17] or damped by spin–spin relaxation [9,18]. This work considers analytical approximations to the radiation damped free precession signal in the presence of symmetric inhomogeneous broadening. Although an analytical theorem relating the initial magnetization tip angle to the tip angle of the central isochromatic vector of a symmetric inhomogeneous distribution after radiation damping ceases was developed, was related to the area of the free precession signal, and was used to predict the formation of a three magnetization component spin echo, the approach was completely devoid of any dynamic information [19–23]. Efforts to include the effects of inhomogeneous broadening into the single isochromatic solution to the non-linear Bloch equations in a perturbative fashion are not useful. In short, time dependent perturbation theory endeavors to expand the inhomogeneous broadening into powers of the free precession time variable. The unfortunate consequence of the expansion is an analytical approximation that diverges on the pulse sequence time scale.

The Dirac, Frenkel, and Maclachlan (DFM) variation of parameters approach was originally developed to provide analytical approximations to the solution of the time dependent Schrödinger equation appropriate for wavepackets colliding on molecular excited state potential energy surfaces [24–28]. Combining these results with recent work that used DFM to model the effects of diffusion on NMR lineshapes produced by spatially non-linear magnetic fields [29] suggests that the DFM variation of parameters may be used to develop analytical approximations for inhomogeneously broadened, radiation damped free precession and echo signals. It is the realization that a symmetric, inhomogeneously broadened NMR line shape can be described with a Gaussian distribution combined with the fact that the contribution of each isochromat to the distribution is identical that makes the DFM approach mathematically tractable in this case. Specifically, expansion of the magnetization inclination angle away from the +z direction and the azimuth angle in terms of powers of the rotating frame offset frequency leads to integrals that can be solved analytically when the inhomogeneous distribution is Gaussian.

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Propagating this mathematical reality through the DFM variation of parameters machinery for the case of an inhomogeneously broadened, radiation damped line shape leads to closed form, non-divergent analytical approximations to free precession and echo signals.

The next section describes the DFM variation of parameters as applied to NMR problems, specifically radiation damping in an inhomogeneously broadened system. After establishing the framework for the calculation of the variation parameters in addition to two ways of evaluating the quality of potential trial function approximate solutions in Section 2, the ability of six trial functions to reproduce the exact dynamics of free induction and echo signals is considered in Section 3. Finally, the DFM based trial functions are used to develop approximations for the recently reported no radiation damping (NORD) pulse sequence [15]. The analytical results are used to describe the reported radiation damping suppression characteristics of the NORD pulse sequence and to suggest an alternative pulse sequence that is less hardware demanding.

2. Theory

The dynamics introduced by inhomogeneous broadening to radiation damped free precession signals can be described by the well-known single isochromat radiation damping problem [3,5]. In the same way that the single isochromat couples to the NMR detection circuit to give a unique current in the rf detection coil, and hence a reaction field, the inhomogeneous distribution $g(\delta)$ defines a set of isochromats with a rotating frame offset frequency δ that separately couple to the properly tuned and matched rf detection coil to yield a single unique reaction field with the

$$H_x = \frac{1}{\gamma T_R M_0}\int u(\delta,t)g(\delta)d\delta = \frac{\langle u(t)\rangle}{\gamma T_R M_0} \tag{1}$$

and

$$H_y = \frac{-1}{\gamma T_R M_0}\int v(\delta,t)g(\delta)d\delta = \frac{-\langle v(t)\rangle}{\gamma T_R M_0} \tag{2}$$

magnetic field components in the x and y direction of the rotating frame respectively. As described in detail in Ref. [5], the transverse field components are written in terms of the transverse time dependent rotating frame isochromatic magnetizations $v(\delta,t)$ and $u(\delta,t)$, the average transverse rotating frame magnetizations $\langle v(t)\rangle$ and $\langle u(t)\rangle$, the equilibrium magnetization M_0, and the radiation damping time constant $(T_R)^{-1} = 2\pi M_0\gamma Q\eta$ where γ is the gyromagnetic ratio, Q is the rf tank circuit figure of merit, and η is the coil filling factor. The offset frequency in the rotating frame introduces the final component of the field $\vec{H} = H_x\hat{i} + H_y\hat{j} + H_z\hat{k}$ as $H_z = \delta/\gamma$. This rotating frame field is used in the Bloch equation $d\vec{M}(\delta,t)/dt = -\gamma\vec{M}(\delta,t)\times\vec{H}$ to develop the isochromatic Bloch equations

$$\frac{d}{dt}M_z(\delta,t) = \frac{\langle v(t)\rangle v(\delta,t) + \langle u(t)\rangle u(\delta,t)}{T_R M_0} \tag{3}$$

$$\frac{d}{dt}v(\delta,t) = -\frac{\langle v(t)\rangle M_z(\delta,t)}{T_R M_0} - \delta u(\delta,t) \tag{4}$$

$$\frac{d}{dt}u(\delta,t) = -\frac{\langle u(t)\rangle M_z(\delta,t)}{T_R M_0} + \delta v(\delta,t) \tag{5}$$

that describe the radiation damping dynamics in an inhomogenoeusly broadened system [5,23].

In direct analogy to Heller's construction of a functional from the time dependent Schrödinger equation [27,28], a similar functional can be developed from the Bloch equations as [29]

$$I(t) = \frac{\int |\frac{d}{dt}\vec{M}(\delta,t) + \gamma\vec{M}(\delta,t)\times\vec{H}|^2 g(\delta)d\delta}{M_0^2}. \tag{6}$$

This form for a functional is particularly useful because the true exact solution to Eqs. (3)–(5) $\vec{M}(\delta,t)$ yields $I(t) = 0$ while approximate forms for the magnetization, in terms of a set of n time dependent parameters $\{\xi_n(t)\}$ as $\vec{M}(\delta,\{\xi_n(t)\})$, yield values $I(t) > 0$. Optimal values for each of the $\xi_n(t)$ parameters can be obtained from Eq. (6) by setting the total variation to zero and introducing the trial function $\vec{M}(\delta,\{\xi_n(t)\})$. In this way n separate coupled equations relating the time derivatives of each $\xi_n(t)$ are obtained as

$$\partial I(t) = 0$$
$$= \frac{\int (\frac{d}{d\xi_m(t)}\vec{M}(\delta,\{\xi_n(t)\}))^{\dagger}\cdot(\frac{d}{dt}\vec{M}(\delta,\{\xi_n(t)\}) + \gamma\vec{M}(\delta,\{\xi_n(t)\})\times\vec{H})g(\delta)d\delta}{M_0^2}. \tag{7}$$

These equations can be used to generate an analytical form for each $\xi_n(t)$ and thus an approximate analytical solution to Eqs. (3)–(5).

The accuracy of a given trial function $\vec{M}(\delta,\{\xi_n(t)\})$, the ability of a given $\vec{M}(\delta,\{\xi_n(t)\})$ to mimic real dynamics, or an estimate of the similarity between $\vec{M}(\delta,\{\xi_n(t)\})$ and the exact solution $\vec{M}(\delta,t)$ is in principle given at each instant in time t by $I(t)$ in Eq. (6). The value of $I(t)$ is identically zero for the exact solution and approaches zero for better approximations of $\vec{M}(\delta,\{\xi_n(t)\})$ to the exact solution. Unfortunately $I(t)$ in its current form delivers an array of numbers, one value at each instant in time. These numbers are difficult to compare in order to determine the best trial function that approximates the exact solution. Realizing that this array of numbers can be collapsed into a single number by integrating as

$$\varepsilon_1 = \int_0^T I(t)dt \tag{8}$$

yields the error ε_1 that can be tracked as a function of the variables that describe the problem. In the case considered here these parameters are the radiation damping time constant, the inhomogeneous distribution characteristics, and the pulse sequence details. The time T in Eq. (8) is taken to be the time that the effects of radiation damping have ceased and only free precession remains [5,19–23].

Another error ε_2 can be defined for a symmetric $g(\delta)$. In the case of free precession following a θ_1 tip angle rf pulse, the analytical theorem [5,19–23]

$$|\Delta\theta_1|_A = \frac{\pi g(0)}{T_R}\sin(\theta_1 - |\Delta\theta_1|_A) \tag{9}$$

describes the $\delta = 0$ central vector tip angle away from the +z direction from its initial θ_1 value to its final $\theta_1 - |\Delta\theta_1|_A$ value at the time T. A similar analytical theorem [5,19–23]

$$|\Delta\theta_2|_A = |\Delta\theta_1|_A + \frac{\pi g(0)}{T_R}\sin(\theta_1 + |\Delta\theta_2|_A - |\Delta\theta_1|_A) \tag{10}$$

was developed for the echo signal with a θ_1 initial tip angle pulse followed by a $\theta_2 = \pi$ rf pulse applied to the free precession signal at the time T. The analytical tip angles $|\Delta\theta_1|_A$ and $|\Delta\theta_2|_A$ are related to the area of the rotating frame magnetization as

$$|\Delta\theta_{m=1,2}|_A = \frac{-1}{M_0 T_R}\int_0^T \langle v(t)\rangle dt, \tag{11}$$

an equation that can be used to develop the tip angle based on the approximate time dependent variation of parameters result as

$$|\Delta\theta_{m=1,2}|_{DFM} = \frac{-1}{M_0 T_R}\int_0^T \langle v(\{\xi_n(t)\})\rangle dt. \tag{12}$$

Care must be taken in the use of Eqs. (11) and (12) to be certain that the $\langle v(t)\rangle$ and $\langle v(\{\xi_n(t)\})\rangle$ magnetizations correspond to the