Journal of Magnetic Resonance 265 (2016) 45–51

Contents lists available at ScienceDirect

Journal of Magnetic Resonance

journal homepage: www.elsevier.com/locate/jmr

Nonadiabatic exchange dynamics during adiabatic frequency sweeps

Thomas M. Barbara

Advanced Imaging Research Center, Oregon Health and Sciences University, Portland, OR 97239, United States

ARTICLE INFO

Article history:
Received 15 November 2015
Revised 7 January 2016
Available online 28 January 2016

Keywords:
Adiabatic sweep
Exchange
Rotating frame relaxation

ABSTRACT

A Bloch equation analysis that includes relaxation and exchange effects during an adiabatic frequency swept pulse is presented. For a large class of sweeps, relaxation can be incorporated using simple first order perturbation theory. For anisochronous exchange, new expressions are derived for exchange augmented rotating frame relaxation. For isochronous exchange between sites with distinct relaxation rate constants outside the extreme narrowing limit, simple criteria for adiabatic exchange are derived and demonstrate that frequency sweeps commonly in use may not be adiabatic with regard to exchange unless the exchange rates are much larger than the relaxation rates. Otherwise, accurate assessment of the sensitivity to exchange dynamics will require numerical integration of the rate equations. Examples of this situation are given for experimentally relevant parameters believed to hold for in-vivo tissue. These results are of significance in the study of exchange induced contrast in magnetic resonance imaging.

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1. Introduction

Over the past decade a substantial effort has been made in exploring the utility of adiabatic frequency sweeps in the study of exchange and relaxation dynamics in magnetic resonance imaging and spectroscopy [1–4]. This approach is an extension of the traditional spin locking methodology in common practice since the first decade of the discovery of NMR, where a constant RF field is applied on or off resonance to create spin locked magnetization, with decay behavior that complemented the measurement of laboratory relaxation time constants [5]. The dynamics of frequency sweeps however, is significantly more complicated than the step wise constant spin locking fields normally used. Although tests for adiabatic evolution with regard to spin dynamics are understood, and adiabatic sweeps easily ensured, the combination of such sweeps in the presence of general conditions of chemical exchange may not be adiabatic with regard to the total dynamics. Only in the simplest cases of fast exchange, where the spin parameters are population weighted averages of the individual site parameters, or very slow exchange, where the exchange can be treated as a first order perturbation, will the conditions for spin dynamic and exchange dynamic, adiabatic behavior coincide. An important exchange scenario is that of isochronous exchange between populations with differing relaxation rate constants [1]. In that case, it is straightforward to obtain general conditions for adiabatic exchange behavior as shown in this work for two site exchange. When these conditions are not met, it is necessary to numerically integrate the dynamic problem using standard algorithms, such as the well-known Runge–Kutta method.

Prior to the analysis for isochronous exchange and the conditions for the measurement of exchange rates during frequency sweeps, it is worthwhile to explore the problem in terms of the Bloch equations for general exchange conditions where the resonance frequency and relaxation rate constants of each site may differ. Though straightforward, a detailed exposition of exchange during a frequency sweep has not appeared in the literature to the best of the author's knowledge. Furthermore, the analysis can guide future experimental work as the use of frequency sweeps expands into a wider range of applications. A useful method for treating relaxation during a frequency swept pulse is offered, as well as new expressions pertinent to the anisochronous, fast exchange limit. The importance of a proper treatment of the inhomogeneous terms are also brought to the foreground. An effort has been made to be complete, even though similar expressions for parts of the analysis have appeared many times in the literature. The approach takes a middle ground with respect to algebraic paucity. For two sites, this is a reasonable compromise that will hopefully serve a broad range of researchers.

2. Bloch equations for frequency sweeps and exchange dynamics

A general method for setting up the spin and exchange dynamics can be accomplished by considering the direct product space of

E-mail address: barbarat@ohsu.edu

http://dx.doi.org/10.1016/j.jmr.2016.01.017
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spin and site labels. For two site exchange considered here, this is a six dimensional space consisting of three magnetization component labels (x,y,z) for each site (a,b). The coupled differential equations for the spin system can then be expressed in the following condensed, block matrix format:

$$\begin{pmatrix}\dot{\boldsymbol{M}}_a\\ \dot{\boldsymbol{M}}_b\end{pmatrix}=\begin{bmatrix}-R_a+H_a(t)-k_a\mathbf{1} & k_b\mathbf{1}\\ k_a\mathbf{1} & -R_b+H_b(t)-k_b\mathbf{1}\end{bmatrix}\begin{pmatrix}\boldsymbol{M}_a\\ \boldsymbol{M}_b\end{pmatrix}+\begin{pmatrix}R_{1a}\boldsymbol{M}_{a0}\\ R_{1b}\boldsymbol{M}_{b0}\end{pmatrix} \tag{1}$$

Here each bold entry signifies the magnetization vector for each site which undergoes evolution and relaxation according to the 3×3 matrices, R_a, $H_a(t)$ and R_b, $H_b(t)$. The exchange dynamics is governed by the rate constants k_a and k_b and the bold $\mathbf{1}$ represents the 3×3 identity matrix. While this block matrix form is not as succinct as pure Kronecker product notation, it serves to illustrate the structure of the dynamics when the adiabatic transformations are imposed in what follows.

The relaxation matrix for site $\alpha = a,b$ can be written in the form

$$R_\alpha=\frac{1}{3}(R_{1\alpha}+2R_{2\alpha})\mathbf{1}+\frac{2}{3}(R_{1\alpha}-R_{2\alpha})\begin{bmatrix}-1/2 & 0 & 0\\ 0 & -1/2 & 0\\ 0 & 0 & 1\end{bmatrix} \tag{2}$$

Eq. (2) has the advantage of clearly displaying the transformation character of the relaxation. For example, the matrix on the right end is the familiar one for a traceless, axially symmetric tensor. Likewise, the spin dynamic matrices are expressed in terms of the standard reduced variables

$$H_\alpha=\Omega_\alpha\begin{bmatrix}0 & \cos\theta_\alpha & 0\\ -\cos\theta_\alpha & 0 & \sin\theta_a\\ 0 & -\sin\theta_a & 0\end{bmatrix} \tag{3}$$

with

$$\Omega_\alpha\cos\theta_\alpha=(\omega_\alpha-\omega(t)) \tag{4}$$

$$\Omega_\alpha\sin\theta_\alpha=\omega_1(t) \tag{5}$$

In these equations, ω_α is the precession frequency of site α, and $\omega(t)$ the time dependent, RF irradiation frequency with amplitude specified by the instantaneous Rabi frequency, $\omega_1(t)$. Complete solutions to the coupled differential equations can only be obtained numerically, especially with time dependent parameters. In the absence of relaxation and exchange, a well-known approach is to design the sweep so that adiabatic evolution is valid [6]. The spin evolution is then dominated by the instantaneous eigenvalues of the spin dynamic variables and adiabatic evolution will hold for the spin dynamics when Ω_α is much larger than the rate of the frequency sweep. For the types of sweep profiles in common use, this implies that Ω_α dominates the relaxation rates as well. It is then straightforward to include relaxation during an adiabatic sweep without an exact solution to the eigenvalues of the matrix $-R_\alpha+H_\alpha(t)$. To an excellent approximation one can use the eigenvalues and eigenvectors of $H_a(t)$ and retain only the diagonal part of R_a in the diagonal basis set of $H_a(t)$.

Therefore, for each site, the diagonal spin dynamics can be written as

$$D_\alpha(t)=\begin{bmatrix}-\rho_{2\alpha}-i\Omega_\alpha & 0 & 0\\ 0 & -\rho_{2\alpha}+i\Omega_\alpha & 0\\ 0 & 0 & -\rho_{1\alpha}\end{bmatrix} \tag{6}$$

Where the rotating frame relaxation rate constants are

$$\rho_{1\alpha}=\frac{1}{3}(R_{1\alpha}+2R_{2\alpha})+\frac{2}{3}(R_{1\alpha}-R_{2\alpha})P_2(\cos\theta_\alpha) \tag{7}$$

$$\rho_{2\alpha}=\frac{1}{3}(R_{1\alpha}+2R_{2\alpha})-\frac{1}{3}(R_{1\alpha}-R_{2\alpha})P_2(\cos\theta_\alpha) \tag{8}$$

and they can be recast into the more familiar form

$$\rho_{1\alpha}=R_{2\alpha}\sin^2\theta_\alpha+R_{1\alpha}\cos^2\theta_\alpha \tag{9}$$

$$\rho_{2\alpha}=\frac{1}{2}R_{2\alpha}+\frac{1}{2}(R_{1\alpha}\sin^2\theta_\alpha+R_{2\alpha}\cos^2\theta_\alpha) \tag{10}$$

These rotating frame relaxation rate constants are equivalent to the expressions derived from rotating frame relaxation theory when the lattice dynamics are characterized by correlation times τ_c such that $\Omega_\alpha\tau_c\ll1$. It is remarkable that they can be obtained from a simple application of first order perturbation theory to the Bloch equations, as contrasted to the usual detailed operator relaxation theory [7] and they should hold generally for any of the usual relaxation mechanisms, as was tested in [8]. It is also noteworthy that this approach can be applied to the recently developed RAFF methods for the measurement of relaxation in fictitious fields, and can provide simple expressions for the effective relaxation rates constants without recourse to the invariant trajectory method [9].

The transformation to the diagonal representation of the spin dynamics is given by the matrix

$$V_\alpha=\begin{bmatrix}\frac{i}{\sqrt{2}}\cos\theta_\alpha & -\frac{i}{\sqrt{2}}\cos\theta_\alpha & \sin\theta_\alpha\\ 1/\sqrt{2} & 1/\sqrt{2} & 0\\ -\frac{i}{\sqrt{2}}\sin\theta_\alpha & \frac{i}{\sqrt{2}}\sin\theta_\alpha & \cos\theta_\alpha\end{bmatrix} \tag{11}$$

The usual test for the adiabatic character of the frequency sweep with respect to the spin dynamics requires that the elements of Eq. (12)

$$\dot{V}_\alpha^{-1}(t)V_{\boldsymbol{\alpha}}(t)=\frac{\dot{\theta}_\alpha}{\sqrt{2}}\begin{bmatrix}0 & 0 & -i\\ 0 & 0 & i\\ -i & i & 0\end{bmatrix} \tag{12}$$

are small in comparison to the magnitude of Ω_α. The adiabatic frame is accomplished by introducing new dependent variables

$$\boldsymbol{N}_\alpha=V_\alpha^{-1}(t)\boldsymbol{M}_\alpha \tag{13}$$

By using Eq. (1) to eliminate $\dot{\boldsymbol{M}}_\alpha$ from $\dot{\boldsymbol{N}}_\alpha=\dot{V}_a^{-1}(t)\boldsymbol{M}_a+V_\alpha^{-1}(t)\dot{\boldsymbol{M}}_\alpha$, the dynamic equations for the $\boldsymbol{N}_\alpha$ become

$$\begin{pmatrix}\dot{\boldsymbol{N}}_a\\ \dot{\boldsymbol{N}}_b\end{pmatrix}=\begin{bmatrix}D_a(t)-\dot{V}_a^{-1}(t)V_{\boldsymbol{a}}(t)-k_a\mathbf{1} & k_bV_a^{-1}(t)V_{\boldsymbol{b}}(t)\\ k_aV_b^{-1}(t)V_a(t) & D_b(t)-\dot{V}_b^{-1}(t)V_{\boldsymbol{b}}(t)-k_b\mathbf{1}\end{bmatrix}\begin{pmatrix}\boldsymbol{N}_a\\ \boldsymbol{N}_b\end{pmatrix}+\begin{pmatrix}R_{1a}V_a^{-1}\boldsymbol{M}_{a0}\\ R_{1b}V_b^{-1}\boldsymbol{M}_{b0}\end{pmatrix} \tag{14}$$

At this point, Eqs. (1) and (14) are equivalent expressions. It is now stipulated that the frequency sweep is adiabatic by requiring that all of the elements of $\dot{V}_a^{-1}(t)V_{\boldsymbol{a}}(t)$ are small relative to the magnitude of $D_a(t)$. Dropping those terms in Eq. (14), the evolution, now adiabatic with respect to the RF sweep, is generated by

$$\begin{pmatrix}\dot{\boldsymbol{N}}_a\\ \dot{\boldsymbol{N}}_b\end{pmatrix}=\begin{bmatrix}D_a(t)-k_a\mathbf{1} & k_bV_a^{-1}(t)V_{\boldsymbol{b}}(t)\\ k_aV_b^{-1}(t)V_a(t) & D_b(t)-k_b\mathbf{1}\end{bmatrix}\begin{pmatrix}\boldsymbol{N}_a\\ \boldsymbol{N}_b\end{pmatrix}+\begin{pmatrix}R_{1a}V_{\boldsymbol{a}}^{-1}\boldsymbol{M}_{a0}\\ R_{1b}V_b^{-1}\boldsymbol{M}_{b0}\end{pmatrix} \tag{15}$$

This condition on the elements of $\dot{V}_a^{-1}(t)V_a(t)$ is the most general condition for adiabatic evolution. An additional caveat is concerned with the possible effects of Berry's phase, which occurs when the diagonal elements of $\dot{V}_a^{-1}(t)V_a(t)$ are nonzero. For frequency sweeps Eq. (12) has no diagonal contributions. A modern

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