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ESTIMATING THE RATIO OF TWO AMPLITUDES IN NUCLEAR MAGNETIC RESONANCE DATA

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ABSTRACT. Probability theory is applied to the problem of estimating the ratio of the amplitudes of two sinusoids in nuclear magnetic resonance data. The posterior probability-density for the amplitude ratio is derived independent of the phase, frequencies, decay-rate constants, variance of the noise, and the amplitude of the other sinusoid. This probability-density function is then applied in an illustrative example, and the results are contrasted with those obtained by traditional analysis.

1. Introduction

Investigating the molecular structure of a compound in a nondestructive manner is difficult. If the nuclei of the compound have a magnetic moment, then one way to investigate the structure is to place the compound in a high magnetic field, excite the system with radio-frequency energy, and listen to it "ring." This type of experiment is called a nuclear magnetic resonance (NMR) experiment. The "ringing" is called a free induction decay (FID). When nuclei of the same type, for example protons, are in different electronic environments (as they are when they are bound to different nuclei) they resonate at slightly different frequencies. These frequencies provide information about the local environments, while the intensities are be related to the relative concentrations of the nuclei.

Traditionally, FID data have been analyzed using the fast Fourier transform after placing zeroes on the end of the FID (i.e., zero-padding the total number of complex points to a power of two). The frequencies are estimated from the real part of the Fourier transform by peak picking, and the amplitudes by integration. After estimating the amplitudes, the ratio is computed. The amplitude ratio is important, because a spectrometer only measures a relative amplitude; not an absolute amplitude.

Bayesian probability theory has recently been applied to the frequency estimation problem [1–4] in NMR, and more recently to amplitude estimation [5,6]. In this paper, probability theory is applied to the problem of determining the amplitudes ratio of the sinusoids. Specifically, the problem is: given that the data contain two exponentially decaying sinusoids with unknown frequencies, decay-rate constants, amplitudes, phases, and variance of the noise, derive the "best" estimate of the ratio of the amplitudes given the data and the prior information. In Bayesian probability theory, all of the information relevant to this question is contained in a probability-density function. This function is independent of the unknown parameters appearing in the model function. Such a probability density function is called a *marginal* probability density function. This marginal posterior probability-density for the amplitude ratio is derived here. The calculation will be for the amplitude ratio of the first sinusoid to the second, but which sinusoid is first and which is second, is a matter of convention; at the end of the calculation the labels on the frequencies and decay-rate constants may be exchanged to obtain the probability-density function for the amplitude ratio of the second sinusoid to the first.

2. The Posterior Probability For The Amplitude Ratio

The problem addressed is: given a quadrature-detected FID containing two in phase exponentially decaying sinusoids with different amplitudes, frequencies, and decay-rate constants, calculate the posterior probability for the amplitude ratio of the sinusoids, independent of all other parameters. In quadrature detected data there are two data sets: the real data (0° phase), and the imaginary data (90° phase). The real data is assumed to be the sum of a signal plus noise:

$$d_R(t_i) = G_R(t_i) + e_i \tag{1}$$

where $d_R(t_i)$ denotes a real data item sampled at time ft$_i$ $(1 \leq i \leq N)$, and $D_R \equiv \{d_R(t_1), \ldots, d_R(t_N)\}$ will denote all of the real data.

The model signal, $G_R(t_i)$, is defined as

$$G_R(t_i) \equiv A_1 \cos(\omega_1 t_i + \theta)\mathrm{e}^{-\alpha_1 t_i} + A_2 \cos(\omega_2 t_i + \theta)\mathrm{e}^{-\alpha_2 t_i} \tag{2}$$

where A_1 is the amplitude of the first sinusoid, A_2 is the amplitude of the second sinusoid, θ is the common phase of the sinusoids, α_1 and α_2 are the decay-rate constants of the sinusoids, and e_i represents noise at time t_i. Note that in phase sinusoids are the rule rather than the exception in NMR FID data.

In addition to the real data, the imaginary data contain the same signal, shifted by 90°:

$$d_I(t_i) = G_I(t_i) + e_i \tag{3}$$

where $d_I(t_i)$ denotes an imaginary data item sampled at time t_i, and all of the imaginary data is represented by $D_I \equiv \{d_I(t_1), \ldots, d_I(t_N)\}$, and D will represent both the real and imaginary data, $D \equiv \{D_R, D_I\}$. The model signal in the imaginary channel is given by

$$G_I(t_i) \equiv -A_1 \sin(\omega_1 t_i + \theta)\mathrm{e}^{-\alpha_1 t_i} - A_2 \sin(\omega_2 t_i + \theta)\mathrm{e}^{-\alpha_2 t_i}. \tag{4}$$

The actual noise, e_i, realized in the imaginary channel is assumed to be different from the noise realized in the real channel. However, the calculation will be simplified by assuming the variance of the noise is the same in both channels.

To proceed, the ratio of the amplitudes must be introduced into the model. Here the ratio of the amplitude of the first sinusoid to the second sinusoid is the quantity of interest:

$$r \equiv \frac{A_2}{A_1}. \tag{5}$$

Introducing the change of variables $rA = A_2$, and $A = A_1$ the model equations are transformed into

$$G_R(t_i) \equiv A[\cos(\omega_1 t_i + \theta)\mathrm{e}^{-\alpha_1 t_i} + r\cos(\omega_2 t_i + \theta)\mathrm{e}^{-\alpha_2 t_i}] \tag{6}$$

for the real channel and

$$G_I(t_i) \equiv -A[\sin(\omega_1 t_i + \theta)\mathrm{e}^{-\alpha_1 t_i} + r\sin(\omega_2 t_i + \theta)\mathrm{e}^{-\alpha_2 t_i}] \tag{7}$$

for the imaginary channel.

In previous work [4,5], it was assumed that a sample of the noise was known. When this sample was present, it placed a scale in the problem against which probability theory could measure small effects. When this sample was not present, the generalized results reduced to those found when no noise sample was gathered [1]. The same strategy will be used here and the more general results will be derived directly. Thus, a noise sample is assumed to be available. The real noise sample is denoted as $D_{\sigma R}$ with $D_{\sigma R} \equiv \{d_{\sigma R}(t_{\sigma 1}), \cdots, d_{\sigma R}(t_{\sigma N_\sigma})\}$. The imaginary noise sample is denoted as $D_{\sigma I}$ with $D_{\sigma I} \equiv \{d_{\sigma I}(t_{\sigma 1}), \cdots, d_{\sigma I}(t_{\sigma N_\sigma})\}$, and $D_\sigma \equiv \{D_{\sigma R}, D_{\sigma I}\}$ denotes both samples. The discrete times $t_{\sigma i} \equiv \{t_{\sigma 1}, \cdots, t_{\sigma N_\sigma}\}$ are assumed distinct from the sampling times for the data D.

The posterior probability for the amplitude ratio will be denoted as $P(r|D_\sigma, D, I)$. According to Bayes' theorem [7], this is given by

$$P(r|D_\sigma, D, I) = \frac{P(r|I)P(D_\sigma, D|r, I)}{P(D_\sigma, D|I)} \tag{8}$$

where $P(r|I)$ is the prior probability for the amplitude ratio, $P(D_\sigma, D|r, I)$ is the joint marginal probability for the data and the noise sample, and $P(D_\sigma, D|I)$ is a normalization constant.

The symbol "I" being carried in these probability functions represents all of the assumptions that go into the calculation; explicitly it represents "everything known about the problem." At present, these include the quadrature nature of the data, the separation of the data into a signal plus additive noise, and that the data is composed of two exponentially decaying sinusoids. These assumptions are hypotheses just like any others appearing inside a probability symbol, and could be tested using the rules of probability theory. However, in this calculation they are assumed known.

3. Assigning Probabilities

Throughout this paper uninformative priors will be used. Normalization will be done at the end of the calculation, and priors ranges for uniform priors will be absorbed into this normalization constant. The first prior to be assigned, $P(r|I)$, will be taken to be a uniform prior $0 \leq r \leq max$ where max is the maximum detectable dynamic range of the digitizer.

Parameter estimation problems using uninformative priors reduce to finding the joint marginal probability for the data and the noise sample (when it is available):

$$P(r|D_\sigma, D, I) \propto P(D_\sigma, D|r, I). \tag{9}$$

The joint marginal probability for the data and the noise sample can be computed from the joint marginal probability for the data, the noise sample, and the parameters:

$$P(r|D_\sigma, D, I) \propto \int AdAd\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_\sigma, D, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2|r, I) \tag{10}$$

where the extra factor, A, is the volume element is due to working in polar coordinates.

The product rule may be used to factor the right-hand-side of this equation into a joint prior for the parameters and a direct probability given the parameters. Assuming the joint prior factors, assigning uniform priors, and dropping all of the prior ranges, one obtains

$$P(r|D_\sigma, D, I) \propto \int AdAd\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_\sigma, D|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \tag{11}$$

as the posterior probability for the amplitudes ratio. Applying the product rule a second time one obtains

$$\begin{aligned} P(r|D_\sigma, D, I) \propto \int & AdAd\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_\sigma|I) \\ & \times P(D|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \end{aligned} \tag{12}$$

where it has been assumed that the noise sample does not depend on the signal parameters: $P(D_\sigma|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = P(D_\sigma|I)$ and it was assumed that the probability for the data sample did not depend on the presence of the noise sample.

The data, D, and the noise sample, D_σ, are actually joint hypotheses. The data, D, stands for both the real, and imaginary data and the noise sample, D_σ, stands for the real and imaginary noise samples. Making this substitution on the right-hand-side of equation (12) one has

$$\begin{aligned} P(r|D_\sigma, D, I) \propto \int & AdAd\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_{\sigma R}, D_{\sigma I}|I) \\ & \times P(D_R, D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \end{aligned} \tag{13}$$

as the posterior probability for the amplitude ratio.

If the product rule is applied to $P(D_{\sigma R}, D_{\sigma I}|I)$, one obtains

$$P(D_{\sigma R}, D_{\sigma I}|I) = P(D_{\sigma R}|I)P(D_{\sigma I}|D_{\sigma R}, I). \tag{14}$$

The two channels of an NMR spectrometer are specifically designed to give projections onto orthogonal functions; the noise in the two channels should be uncorrelated. Having no reason to assume dependence, it will be assumed that $P(D_{\sigma I}|D_{\sigma R}, I) = P(D_{\sigma I}|I)$ and the posterior probability for the amplitude ratio becomes

$$\begin{aligned} P(r|D_\sigma, D, I) \propto \int & AdAd\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_{\sigma R}|I)P(D_{\sigma I}|I) \\ & \times P(D_R, D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I). \end{aligned} \tag{15}$$

Applying the product rule to $P(D_R, D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I)$, one obtains

$$\begin{aligned} P(D_R, D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = & P(D_R|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \\ & \times P(D_I|D_R, r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I). \end{aligned} \tag{16}$$

Again the NMR spectrometer is designed so that the two channels give independent uncorrelated measurements of the signal. Because the measurements are independent, the probability for the imaginary data should reflect this information and be independent of the real data and vice versa. With these assumptions the joint probability of the data factors and

$$
\begin{aligned}
P(D_R, D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = P(D_R|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \\
\times P(D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I).
\end{aligned}
\tag{17}
$$

The posterior probability for the amplitude ratio is given by

$$
\begin{aligned}
P(r|D_\sigma, D, I) \propto \int AdAd\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_{\sigma R}|I)P(D_{\sigma I}|I) \\
\times P(D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I)P(D_R|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I)
\end{aligned}
\tag{18}
$$

where $P(D_R|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I)$ is the direct probability for the real data, and the direct probability for the imaginary data is $P(D_I|r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I)$.

The posterior probability for the amplitude ratio has now been sufficiently simplified to permit assignment of the various terms. To do this assignment, note that equations (1) and (3) constitute a definition of what is meant by noise in this calculation. The direct probability for the data given the parameters *is* the noise prior probability given the parameters. Before these probability-density functions can be assigned, one must assign a prior probability for the noise. To do this the assumptions made about the noise must be explicitly stated. As in previous works [1–4,8] it will be assumed that the noise carries a finite, but unknown total power. Using this assumption in a maximum entropy calculation [9] results in the assignment of a Gaussian for the noise prior probability-density:

$$
P(e_1, \cdots, e_N|\sigma, I) = (2\pi\sigma^2)^{-\frac{N}{2}} \exp\left\{-\sum_{i=1}^{N} \frac{e_i^2}{2\sigma^2}\right\}. \tag{19}
$$

The direct probability for obtaining the real data is given by

$$
P(D_R|\sigma, r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = (2\pi\sigma^2)^{-\frac{N}{2}} \exp\left\{-\sum_{i=1}^{N} \frac{[d_R(t_i) - G_R(t_i)]^2}{2\sigma^2}\right\} \tag{20}
$$

where the notation has been adjusted as follows: first, $e_1, \cdots, e_N$, were replaced by D_R to indicate that it is the direct probability for the real data; and second σ, the standard deviation for the noise, was added to the probability-density function to indicate that it is a known quantity. Later, the product rule and sum rules of probability theory will be used to remove the dependence on the standard deviation σ. The direct probability for obtaining the imaginary data is given by

$$
P(D_I|\sigma, r, A, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = (2\pi\sigma^2)^{-\frac{N}{2}} \exp\left\{-\sum_{i=1}^{N} \frac{[d_I(t_i) - G_I(t_i)]^2}{2\sigma^2}\right\}. \tag{21}
$$

The direct probability for the real noise sample is given by

$$
P(D_{\sigma R}|\sigma, I) = (2\pi\sigma^2)^{-\frac{N_\sigma}{2}} \exp\left\{-\sum_{i=1}^{N_\sigma} \frac{d_R(t_i)^2}{2\sigma^2}\right\}. \tag{22}
$$

Last, the direct probability for the imaginary noise sample is given by

$$P(D_{\sigma I}|\sigma, I) = (2\pi\sigma^2)^{-\frac{N_\sigma}{2}} \exp\left\{-\sum_{i=1}^{N_\sigma} \frac{d_I(t_i)^2}{2\sigma^2}\right\}. \tag{23}$$

Combining these four terms, the posterior probability for the amplitude ratio is given by

$$\begin{aligned} P(r|\sigma, D_\sigma, D, I) \propto \int dA A dA d\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 \sigma^{-2N-2N_\sigma} \exp\left\{-\frac{2N\overline{d^2} + 2N_\sigma \overline{d_\sigma^2}}{2\sigma^2}\right\} \\ \times \exp\left\{\frac{2A[R_1\cos(\theta) - I_1\sin(\theta) + rR_2\cos(\theta) - rI_2\sin(\theta)]}{2\sigma^2}\right\} \\ \times \exp\left\{-\frac{A^2[C_{11} + 2rC_{12} + r^2C_{22}}{2\sigma^2}\right\} \end{aligned} \tag{24}$$

where

$$R_x \equiv R(\omega_x, \alpha_x) \qquad \text{with } x = 1 \text{ or } 2, \tag{25}$$

and

$$C_{jk} \equiv C(\omega_j - \omega_k, \alpha_j + \alpha_k) \qquad \text{with } j \text{ and } k = 1 \text{ or } 2 \tag{26}$$

and similarly for I_x and S_{jk}.

In obtaining the above, the identity $\sin^2(x) + \cos^2(x) = 1$, and the trigonometric relations for the sum of two angles were used. The mean-square of the data value, $\overline{d^2}$, is defined as

$$\overline{d^2} \equiv \frac{1}{2N} \sum_{i=1}^{N} d_R(t_i)^2 + d_I(t_i)^2. \tag{27}$$

The mean-square of noise value, $\overline{d_\sigma^2}$, is defined as

$$\overline{d_\sigma^2} \equiv \frac{1}{2N_\sigma} \sum_{i=1}^{N_\sigma} d_{\sigma R}(t_i)^2 + d_{\sigma I}(t_i)^2. \tag{28}$$

And the notation "$\cdot$" means the two functions of discrete times are to be multiplied and a sum over discrete times performed, for example:

$$d_R \cdot \cos(\omega t + \theta)\mathrm{e}^{-\alpha t} \equiv \sum_{i=1}^{N} d_R(t_i)\cos(\omega t_i + \theta)\mathrm{e}^{-\alpha t_i}. \tag{29}$$

The functions $R(\omega, \alpha)$ and $I(\omega, \alpha)$ are defined as

$$R(\omega, \alpha) \equiv d_R \cdot \cos(\omega t)\mathrm{e}^{-\alpha t} - d_I \cdot \sin(\omega t)\mathrm{e}^{-\alpha t} \tag{30}$$

and

$$I(\omega, \alpha) \equiv d_R \cdot \sin(\omega t)\mathrm{e}^{-\alpha t} + d_I \cdot \cos(\omega t)\mathrm{e}^{-\alpha t}. \tag{31}$$

When the data are uniformly sampled and ω is taken on a discrete grid, $\omega_i = 2\pi i/N$ $(i = 0, 1, \cdots, N-1)$, the functions $R(\omega_i, \alpha)$ and $I(\omega_i, \alpha)$ are the real and imaginary parts of the fast Fourier transform of the complex FID data when the data have been multiplied by a decaying exponential of decay-rate α. The function $C(\omega, \alpha)$ is defined as

$$C(\omega, \alpha) \equiv \sum_{i=1}^{N} \cos(\omega t_i) \mathrm{e}^{-\alpha t_i}. \tag{32}$$

If uniform sampling is used, then $C(\omega, \alpha)$ may be expressed in closed form. Taking the sampling times to be $t_i = \{0, 1, \cdots, N-1\}$, then the frequencies and decay-rate constants are measured in radians and the sum, appearing in $C(\omega, \alpha)$, may be done explicitly to obtain

$$C(\omega, \alpha) = \frac{1 - \cos(\omega)\mathrm{e}^{-\alpha} - \cos(N\omega)\mathrm{e}^{-N\alpha} + \cos[(N-1)\omega]\mathrm{e}^{-(N+1)\alpha}}{1 - 2\cos(\omega)\mathrm{e}^{-\alpha} + \mathrm{e}^{-2\alpha}}. \tag{33}$$

If nonuniform sampling is being used, $C(\omega, \alpha)$, $R(\omega, \alpha)$, and $I(\omega, \alpha)$ must be computed from their definitions.

4. Removing Nuisance Parameters

There are seven nuisance parameters: two frequencies ω_1 and ω_2, two decay-rate constants, α_1 and α_2, one phase θ, amplitudes, A, and the variance of the noise, σ. The two frequencies and decay-rate constants appear in the posterior in a nonlinear way and the integrals over these parameters cannot be done explicitly; approximations for the integrals will be used. The remaining integrals may be done in closed form.

To evaluate the integral over the phase, one uses the relationship

$$a\cos(x) + b\sin(x) = \sqrt{a^2 + b^2}\cos(x + \chi) \quad \text{where} \quad \chi = \tan^{-1}(b/a). \tag{34}$$

This relationship transforms the θ integral into an integral representation of the Bessel function of a real argument I_0:

$$\begin{aligned} P(r|\sigma, D_\sigma, D, I) \propto \int & AdAd\omega_1 d\omega_2 d\alpha_1 d\alpha_2 \sigma^{-2N-2N_\sigma+2} \\ & \times \exp\left\{-\frac{2N\overline{d^2} + 2N_\sigma\overline{d_\sigma^2} + A^2 X}{2\sigma^2}\right\} I_0\left(\frac{AY}{\sigma^2}\right) \end{aligned} \tag{35}$$

where

$$X \equiv C_{11} + 2rC_{12} + r^2 C_{22}, \tag{36}$$

and

$$Y \equiv \sqrt{[R_1 + rR_2]^2 + [I_1 + rI_2]^2}. \tag{37}$$

The amplitude integral may be evaluated by using the following integral relation

$$\int_0^\infty dx x \mathrm{e}^{-ax^2} I_0(bx) = \frac{1}{2a}\exp\left\{-\frac{b^2}{4a}\right\}. \tag{38}$$

Evaluating this integral one obtains:

$$P(r|\sigma, D_\sigma, D, I) \propto \int d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 \frac{\sigma^{-2N-2N_\sigma+2}}{X} \exp\left\{-\frac{2N\overline{d^2} + 2N_\sigma \overline{d_\sigma^2} - X^2/Y}{2\sigma^2}\right\} \quad (39)$$

as the posterior probability for the amplitude ratio.

The standard deviation, σ, is the only remaining parameters that may be removed in closed form. Before doing so, note that the frequencies appear in the integral in the form of $[R(\omega_1, \alpha_1) + rR(\omega_2, \alpha_2)]^2$ $[I(\omega_x, \alpha_x) + rI(\omega_2, \alpha_2)]^2$. If one considers this quantity as a function of ω_1, and holds the other parameters constant, then it is varying like a power spectrum. Power spectra often change by many orders of magnitude over a small frequency range and it is the *exponential* of this quantity that is being computed. Assuming even moderate signal-to-noise (frequency domain peak signal-to-noise RMS noise ratio of at least 2 or 3), this frequency integral is well approximated by a delta function. The same argument applies equally well to the integral over ω_2.

The integrals over the decay-rate constants are similar. The function $R(\omega_1, \alpha_1)$, $I(\omega_1, \alpha_1)$ are the the real and imaginary parts of the discrete Fourier transform of the complex FID data when an exponential filter is applied. When this exponential is decaying at the same rate as the first sinusoid, the filter is "matched" and small changes in the decay rate constant will make large changes in the height of the posterior probability. Similarly for $R(\omega_2, \alpha_2)$ and $I(\omega_2, \alpha_2)$. At these matched values, small changes in exponential decay rate constants will cause corresponding large changes in the height of the posterior, and again the integrals may be approximated by delta functions. Designating $\hat{\omega}_1$, $\hat{\alpha}_1$, $\hat{\omega}_2$, and $\hat{\alpha}_2$ as the values that maximize the joint posterior probability for the frequencies and decay-rate constants (the matched values), the posterior probability for the amplitude ratio is approximately given by

$$P(r|\sigma, D_\sigma, D, I) \approx \int d\sigma \frac{\sigma^{-2N-2N_\sigma+2}}{X} \exp\left\{-\frac{2N\overline{d^2} + 2N_\sigma \overline{d_\sigma^2} - X^2/Y}{2\sigma^2}\right\}\Bigg|_{\hat{\omega}_1\hat{\omega}_2\hat{\alpha}_1\hat{\alpha}_2}. \quad (40)$$

The last to remove the standard deviation of the noise, note that

$$P(r|D_\sigma, D, I) = \int d\sigma P(r, \sigma|D_\sigma, D, I) = \int P(\sigma|I) P(r|\sigma, D_\sigma, D, I). \quad (41)$$

Using a Jeffreys prior [9,10] for the standard deviation $(1/\sigma)$ and evaluating the integral over σ one obtains

$$P(r|D_\sigma, D, I) \propto \int \frac{d\omega_1 d\omega_2 d\alpha_1 d\alpha_2}{X} \left[1 - \frac{X^2}{Y(2N\overline{d^2} + 2N_\sigma \overline{d_\sigma^2})}\right]^{1-N-N_\sigma}. \quad (42)$$

Substituting the definitions X and Y Eq. (36,37) one obtains

$$P(r|D_\sigma, D, I) \propto X^{-1} \left[1 - \frac{(R_1 + rR_2)^2 + (I_1 + rI_2)^2}{(C_{11} + 2rC_{12}r^2 C_{22})(2N\overline{d^2} + 2N_\sigma \overline{d_\sigma^2})}\right]^{3-N-N_\sigma}\Bigg|_{\hat{\omega}_1\hat{\omega}_2\hat{\alpha}_1\hat{\alpha}_2} \quad (43)$$

as the posterior probability for the amplitude ratio.

5. Example

To illustrate the use of the previous calculation, consider Fig. 1A. This is a plot of the real part of the fast Fourier transform for computer-generated FID containing two exponentially decaying sinusoids. The data for the real channel (0°) were generated from

$$d_R(T_i) = 100\cos(\omega_1 t_i)\mathrm{e}^{-\alpha_1 t_i} + 200\cos(\omega_2 t_i)\mathrm{e}^{-\alpha_2 t_i} + e_i \tag{44}$$

where e_i represents a random Gaussian noise component of standard deviation one. The imaginary data (90°) were generated from the same equation, except the sinusoids are shifted by 90°. For data taken every millisecond for 2.048 seconds, there are $N = 2048$ points in the real and imaginary channel. The frequencies and decay-rate constants are given by

$$\omega_1 = 47.7 \quad \text{Hz and} \quad \alpha_1 = 1.6 \text{ Hz} \tag{45}$$

$$\omega_2 = 55.7 \quad \text{Hz and} \quad \alpha_2 = 16 \text{ Hz}. \tag{46}$$

The peak amplitude to RMS signal-to-noise ratio is large; nonetheless, because of overlap, traditional methods can not be estimate the amplitudes, so no estimate of the amplitude ratio is available. Using traditional methods, the amplitudes are estimated by integrating the areas under the peaks in the absorption spectrum; unless these peaks are well separated, the integral estimates the combined area.

To apply the previous calculation, one must first locate the maximum of the posterior probability for the frequencies and decay-rate constants. This is done using the procedures described in [3]. After locating these values, one can estimate the amplitudes ratio by computing the posterior probability for the amplitudes ratio using Eq. (43). The resulting probability-density functions are shown in Figs. 1B and C. Notice that both amplitude ratios have been well determined using Bayesian methods.

For the ratio of the amplitude of the sinusoid at frequency 47.7 Hertz to the sinusoid at 55.7 Hertz the ratio is estimated to be 2.003 ± 0.006 at one standard deviation, where by standard deviation it is meant the smallest area that encloses 63% of the total probability. The reciprocal ratio, i.e., the ratio of the amplitude of the sinusoid at 55.7 Hz divided by the amplitude of the sinusoid at 47.7 Hz is 0.499 ± 0.017 at one standard deviation. The true values are 2 and one half respectively.

6. Summary And Conclusions

Probability theory has been successfully applied to the problem of estimating the amplitude ratio in NMR FID data when the data containing two sinusoids of different amplitudes, frequencies, decay-rate constants and the same phase. The posterior probability for the ratio of the amplitudes, independent of the values of all the other parameters was computed. An example illustrating that probability theory can easily estimate amplitude ratios under conditions where traditional discrete Fourier transform methods fail was given.

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Figure 1: Estimation of the Amplitude Ratio

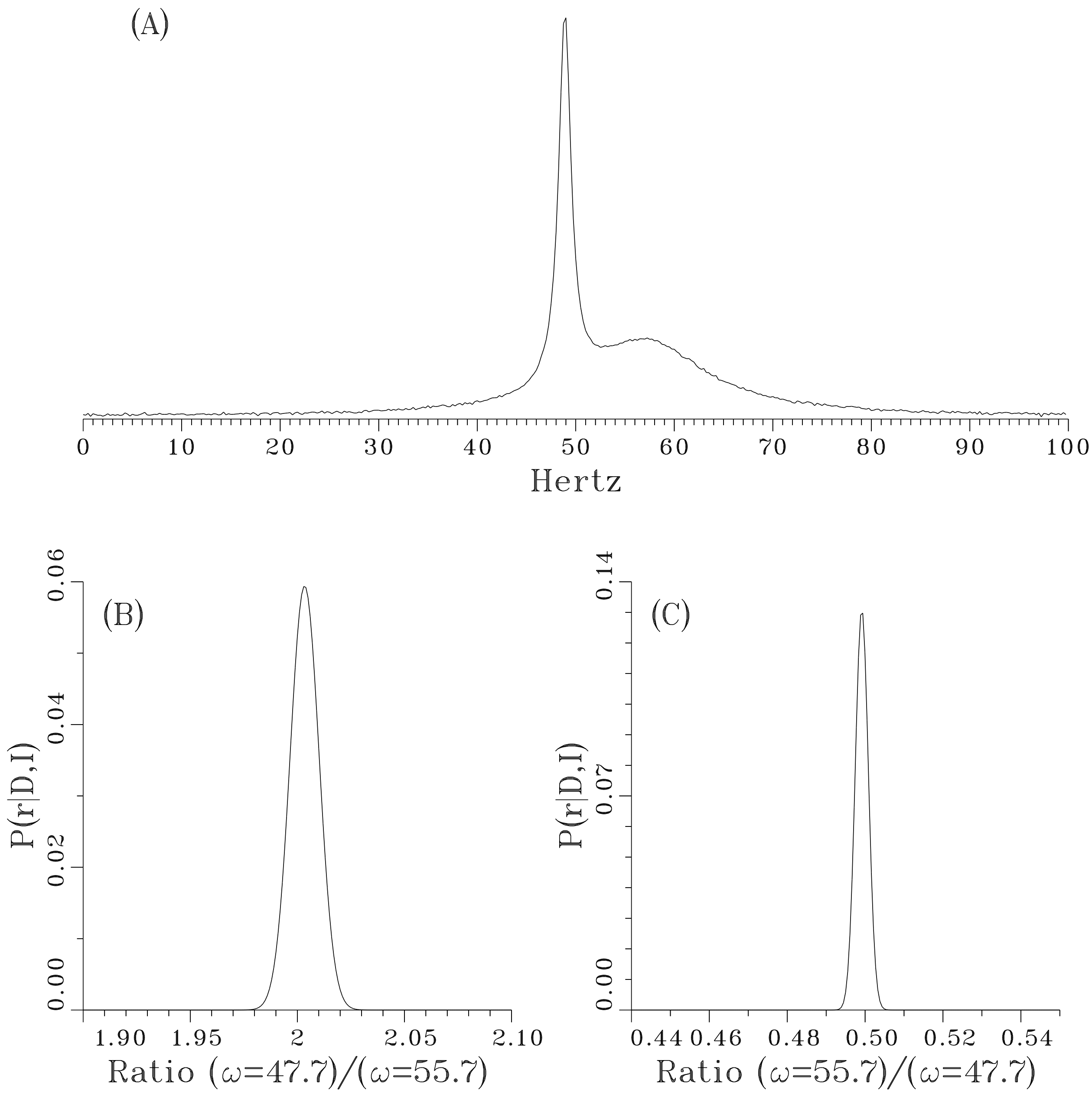

Fig. 1A is the absorption spectrum (the real part of the Fourier transform) of the computer simulated FID data. Traditional methods cannot estimate either the frequencies or the amplitudes of the sinusoids due to the overlap exhibited by the two NMR resonances. Panel B is the posterior probability for ratio of the amplitudes of the sinusoids at frequency 47.7 Hz to the sinusoid at 55.7 Hz. Panel C is the posterior probability for the reciprocal. The true ratios are 2 and one half respectively.

REFERENCES

Bretthorst, G. Larry, "Bayesian Analysis. I. Parameter Estimation Using Quadrature NMR Models," *J. Magn. Reson.,* **88**, pp. 533-551 (1990).

Bretthorst, G. Larry, "Bayesian Analysis. II. Model Selection," *J. Magn. Reson.,* **88**, pp. 552-570 (1990).

Bretthorst, G. Larry, "Bayesian Analysis. III. Applications to NMR Signal Detection, Model Selection and Parameter Estimation," *J. Magn. Reson.,* **88**, pp. 571-595 (1990).

Bretthorst, G. Larry, "Bayesian Analysis. IV. Noise and Computing Time Considerations," *J. Magn. Reson.,* June 15, (1991).

Bretthorst, G. Larry, "Bayesian Analysis. V. Amplitude Estimation, The One Frequency Model," submitted *J. Magn. Reson.,*.

Bretthorst, G. Larry, "Amplitude Estimation In Nuclear Magnetic Resonance Data," in the Proceedings of the Third Valencia Conference on Bayesian Statistics (J. Bernardo *ed*), in press.

Rev. T. Bayes, *Philos. Trans. R. Soc. London* **53,** 370 (1763); reprinted in *Biometrika* **45,** 293 (1958), and "Facsimiles of Two Papers by Bayes," with commentary by W. Edwards Deming Hafner, New York, 1963.

Bretthorst, G. Larry, *Bayesian Spectrum Analysis and Parameter Estimation,* in "Lecture Notes in Statistics" **48,** Springer-Verlag, New York, New York, 1988.

Jaynes, E. T., " Papers on Probability, Statistics and Statistical Physics" R. D. Rosenkrantz, *ed.,* D. Reidel, Dordrecht, The Netherlands, 1983.

Jeffreys, H., "Theory of Probability," Oxford University Press, London, 1939; Later editions, 1948, 1961.