

## AMPLITUDE ESTIMATION IN NUCLEAR MAGNETIC RESONANCE DATA

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*ABSTRACT:* Probability theory is applied to the problem of estimating the amplitudes of the sinusoids in nuclear magnetic resonance data containing two exponentially decaying sinusoids. The posterior probability-density of one of the amplitudes is derived independent of the phases, 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 techniques.

### Introduction

Investigating the molecular structure of a compound in a nondestructive manner is difficult. If the nuclei of the compound have a magnetic moments, 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.

Traditionally, FID data have been analyzed using the fast Fourier transform after placing zero’s 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. The real part of the discrete Fourier transform is called the absorption spectrum.

Bayesian probability theory has recently been applied to the frequency estimation problem [1–4] in NMR. In this paper probability theory is applied to the problem of determining the amplitudes 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 amplitude for one of the sinusoids. In Bayesian probability theory, all of the information relevant to this question is contained in a probability-density function, which is independent of the unknown parameters appearing in the model function.

The marginal posterior probability-density for the amplitude of one of the sinusoids is derived using the rules of probability theory. The calculation will be for the amplitude of

the first sinusoid, 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 of the second sinusoid.

## The Posterior Probability For The Amplitude

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

$$d_R(t_i) = G_R(t_i) + e_i \quad (1)$$

where  $d_R(t_i)$  denotes a real data item sampled at time  $t_i$  ( $1 \leq i \leq N$ ). The model signal  $G_R(t_i)$  is defined as

$$G_R(t_i) \equiv A \cos(\omega_1 t_i + \theta) e^{-\alpha_1 t_i} + [A_3 \cos(\omega_2 t_i) + A_4 \sin(\omega_2 t_i)] e^{-\alpha_2 t_i} \quad (2)$$

where  $A$  is the amplitude of the sinusoid to be estimated,  $\theta$  is the phase of the sinusoid,  $A_3$  and  $A_4$  are the amplitudes of the sine and cosine components of the second sinusoid,  $\alpha_1$  and  $\alpha_2$  are the decay-rate constants of the sinusoids, and  $e_i$  represents noise at time  $t_i$ . Notice that the two sinusoids have been represented in different but mathematically equivalent forms. The sinusoid of frequency  $\omega_1$  has been written in polar coordinates, while the other sinusoid was written in cartesian coordinates. This was done for computational convenience, the integrals to be performed are easier this way. The real data will be denoted as  $D_R \equiv \{d_R(t_1), \dots, d_R(t_N)\}$ . The seven parameters  $A_3$ ,  $A_4$ ,  $\theta$ ,  $\omega_1$ ,  $\omega_2$ ,  $\alpha_1$  and  $\alpha_2$  are considered as nuisance parameters and are not to appear in the final posterior probability-density function. In addition to the real data, the imaginary data contain the same signal, except shifted by  $90^\circ$ :

$$d_I(t_i) = G_I(t_i) + e_i \quad (3)$$

where  $d_I(t_i)$  denotes an imaginary data item sampled at time  $t_i$ . The model signal in the imaginary channel,  $G_I(t_i)$ , is the same as the real signal, except for a  $90^\circ$  phase shift:

$$G_I(t_i) \equiv -A \sin(\omega_1 t_i + \theta) e^{-\alpha_1 t_i} - [A_3 \sin(\omega_2 t_i) - A_4 \cos(\omega_2 t_i)] e^{-\alpha_2 t_i}. \quad (4)$$

The imaginary data will be denoted as  $D_I \equiv \{d_I(t_1), \dots, d_I(t_N)\}$ . 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 prior information about the noise is assumed to be the same in both channels. That is, if the noise variance is  $\sigma$  in the real channel, then there is no reason to believe it differs from  $\sigma$  in the imaginary channel.

The posterior probability for the amplitude will be denoted as  $P(A|D_R, D_I, I)$ . According to Bayes' theorem [6], this is given by

$$P(A|D_R, D_I, I) = \frac{P(A|I)P(D_R, D_I|A, I)}{P(D_R, D_I|I)} \quad (5)$$

where  $P(A|I)$  is the prior probability for the amplitude of the first sinusoid,  $P(D_R, D_I|A, I)$  is the joint direct probability for the real and imaginary data, and  $P(D_R, D_I|I)$  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 in a probability symbol, and could be tested using the rules of probability theory. However, in this case they are assumed known.

## Assigning Probabilities

Throughout this paper uninformative priors will be used. Normalization will be done at the end of the calculation, so constant priors will be absorbed into this normalization constant. The first prior to be assigned,  $P(A|I)$ , will be taken to be a uniform prior and ignored. Parameter estimation problems using uninformative priors always reduce to finding the direct probability:

$$P(A|D_R, D_I, I) \propto P(D_R, D_I|A, I). \quad (6)$$

The direct probability can be computed from the joint probability for the data and the parameters:

$$P(A|D_R, D_I, I) \propto \int dA_3 dA_4 d\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_R, D_I, A_3, A_4, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2|A, I). \quad (7)$$

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 and assigning uniform priors to all of the individual priors results in

$$P(A|D_R, D_I, I) \propto \int dA_3 dA_4 d\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_R, D_I|A, A_3, A_4, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \quad (8)$$

as the posterior probability for the amplitudes. Last, applying the product rule, and assuming that the probability for the real data is independent of the imaginary data, one obtains

$$P(A|D_R, D_I, I) \propto \int dA_3 dA_4 d\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 P(D_R|A, A_3, A_4, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) \quad (9)$$

$$\times P(D_I|A, A_3, A_4, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I).$$

The posterior probability for the amplitude has now been sufficiently simplified to permit assignment of the various terms. To do this assignment, notice 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, 2, 3, 4, 7] 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:

$$P(e_1, \dots, e_N | \sigma, I) = (2\pi\sigma^2)^{-\frac{N}{2}} \exp \left\{ -\sum_{i=1}^N \frac{e_i^2}{2\sigma^2} \right\}. \quad (10)$$

Thus the direct probability for obtaining the real data is given by

$$P(D_R | \sigma, A, A_3, A_4, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = (2\pi\sigma^2)^{-\frac{N}{2}} \exp \left\{ -\sum_{i=1}^N \frac{[d_R(t_i) - G_R(t_i)]^2}{2\sigma^2} \right\} \quad (11)$$

where the notation has been adjusted as follows: first,  $e_1, \dots, e_N$ , were replaced by  $D_R$  to indicate it is the direct probability for the real data; and second  $\sigma$ , 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  $\sigma$ . The direct probability for obtaining the imaginary data is given by

$$P(D_I | \sigma, A, A_3, A_4, \theta, \omega_1, \omega_2, \alpha_1, \alpha_2, I) = (2\pi\sigma^2)^{-\frac{N}{2}} \exp \left\{ -\sum_{i=1}^N \frac{[d_I(t_i) - G_I(t_i)]^2}{2\sigma^2} \right\}. \quad (12)$$

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

$$\begin{aligned} P(A | \sigma, D, I) &\propto \int dA_3 dA_4 d\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 \sigma^{-2N} \exp \left\{ -\frac{2N\bar{d}^2}{2\sigma^2} \right\} \\ &\times \exp \left\{ \frac{2[AR_1 \cos(\theta) - AI_1 \sin(\theta) + A_3R_2 + A_4I_2]}{2\sigma^2} \right\} \\ &\times \exp \left\{ -\frac{2AA_3[C_{12} \cos(\theta) - S_{12} \sin(\theta)]}{2\sigma^2} \right\} \\ &\times \exp \left\{ \frac{2AA_4[C_{12} \cos(\theta) + S_{12} \sin(\theta)]}{2\sigma^2} \right\} \\ &\times \exp \left\{ -\frac{[A^2C_{11} + A_3^2C_{22} + A_4^2C_{22}]}{2\sigma^2} \right\} \end{aligned} \quad (13)$$

where

$$R_x \equiv R(\omega_x, \alpha_x) \quad (14)$$

and

$$C_{jk} \equiv C(\omega_j - \omega_k, \alpha_j + \alpha_k) \quad (15)$$

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,  $\bar{d}^2$ , is defined as

$$\bar{d}^2 \equiv \frac{1}{2N} \sum_{i=1}^N d_R(t_i)^2 + d_I(t_i)^2 \quad (16)$$

where the notation “.” means the functions are to be multiplied and a sum over discrete times performed. For example:

$$d_R \cdot \cos(\omega t + \theta) e^{-\alpha t} \equiv \sum_{i=1}^N d_R(t_i) \cos(\omega t_i + \theta) e^{-\alpha t_i}. \quad (17)$$

The functions  $R(x, y)$  and  $I(x, y)$  are defined as

$$R(x, y) \equiv d_R \cdot \cos(xt) e^{-yt} - d_I \cdot \sin(xt) e^{-yt} \quad (18)$$

and

$$I(x, y) \equiv d_R \cdot \sin(xt) e^{-yt} + d_I \cdot \cos(xt) e^{-yt}. \quad (19)$$

When the data are uniformly sampled and  $x$  is taken on a discrete grid,  $x = 2\pi i/N$  ( $i = 0, 1, \dots, N-1$ ), the functions  $R(x_i, y)$  and  $I(x_i, y)$  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  $y$ . The function  $C(x, y)$  is defined as

$$C(x, y) \equiv \sum_{i=1}^N \cos(xt_i) e^{-yt_i}. \quad (20)$$

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

$$C(x, y) = \frac{1 - \cos(x) e^{-y} - \cos(Nx) e^{-Ny} + \cos[(N-1)x] e^{-(N+1)y}}{1 - 2 \cos(x) e^{-y} + e^{-2y}}. \quad (21)$$

Similarly,  $S(x, y)$  is defined as

$$S(x, y) \equiv \sum_{i=1}^N \sin(xt_i) e^{-yt_i}, \quad (22)$$

and if uniform sampling is used  $S(x, y)$  may be summed explicitly to obtain

$$S(x, y) = \frac{\sin(x) e^{-y} - \sin(Nx) e^{-Ny} + \sin[(N-1)x] e^{-(N+1)y}}{1 - 2 \cos(x) e^{-y} + e^{-2y}}. \quad (23)$$

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

## Removing Nuisance Parameters

There are eight nuisance parameters: two frequencies  $\omega_1$  and  $\omega_2$ , two decay-rate constants,  $\alpha_1$  and  $\alpha_2$ , one phase  $\theta$ , two amplitudes,  $A_3$  and  $A_4$ , and the variance of the noise,  $\sigma$ . 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 will be used. The

remaining parameters can be removed by integration. Although it is not necessary, it will be convenient to use an approximation in removing the standard deviation of the noise.

The amplitudes  $A_3$  and  $A_4$  appear in the exponent as quadratics. Thus the integrals are Gaussian integrals. The range on the integrals is from  $-\infty$  to  $\infty$  and they may be evaluated easily in closed form. One obtains:

$$\begin{aligned}
P(A|\sigma, D, I) &\propto \int d\theta d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 \sigma^{-2N+2} \exp\left\{-\frac{2N\bar{d}^2}{2\sigma^2}\right\} \\
&\times \exp\left\{\frac{2A[R_1 \cos(\theta) - I_1 \sin(\theta)] - A^2 C_{11}}{2\sigma^2}\right\} \\
&\times \exp\left\{\frac{R_2^2 + I_2^2 + A^2(S_{12}^2 + C_{12}^2)}{2C_{22}\sigma^2}\right\} \\
&\times \exp\left\{\frac{2A(I_2 S_{12} - R_2 C_{12}) \cos(\theta)}{2C_{22}\sigma^2}\right\} \\
&\times \exp\left\{\frac{2A(I_2 C_{12} + R_2 S_{12}) \sin(\theta)}{2C_{22}\sigma^2}\right\}
\end{aligned} \tag{24}$$

as the posterior probability for the amplitude.

Removing the phase  $\theta$  is a little more difficult. The limits on this integral are from 0 to  $2\pi$ . To evaluate the integral one uses the relationship

$$a \cos(x) + b \sin(x) = \sqrt{a^2 + b^2} \cos(x + \chi) \quad \text{where} \quad \chi = \tan^{-1}(b/a). \tag{25}$$

This relationship transforms the  $\theta$  integral into an integral representation of the  $I_0$  Bessel function:

$$P(A|\sigma, D, I) \propto \int d\omega_1 d\omega_2 d\alpha_1 d\alpha_2 \sigma^{-2N+2} \exp\left\{-\frac{2N\bar{d}^2 - X + ZA^2}{2\sigma^2}\right\} I_0\left(\frac{AY}{\sigma^2}\right) \tag{26}$$

where

$$X \equiv \frac{R_2^2 + I_2^2}{C_{22}}, \tag{27}$$

$$Y \equiv \frac{C_{11}C_{22} - C_{12}^2 - S_{12}^2}{C_{22}}, \tag{28}$$

and

$$Z \equiv C_{22}^{-1} \sqrt{[R_1 C_{22} + I_2 S_{12} - R_2 C_{12}]^2 + [I_1 C_{22} - I_2 C_{12} - R_2 S_{12}]^2}. \tag{29}$$

With the exception of the standard-deviation integral, none of the remaining integrals can be done exactly. Although, the standard-deviation integral can be evaluated in closed form, the resulting expression is too complex to be useful. Instead, approximations will be used. Similar approximations will be made in evaluating the integrals over the frequencies and decay rate constants. It will be assumed that the posterior probability is so sharply peaked as a function of these parameters that the integrals are reasonable representations of delta function integrals. To motivate this approximation, notice that the frequencies appear

in the integral in the form of  $R(\omega_x, \alpha_x)^2$  plus  $I(\omega_x, \alpha_x)^2$ . These terms are the exponential of the complex power spectrum of the FID data. Power spectra often changes by many orders of magnitude over a small frequency range and it is the *exponential* of this quantity that is being computed. Therefore, the frequency integrals are well approximated by delta function. The integrals over the decay-rate constants are similar. When the decay-rate constants are equal to the true values, these functions are the matched filter for the FID data. As with frequencies, small changes in decay-rates 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 posterior probability for the amplitude is approximately given by

$$P(A|\sigma, D, I) \approx \sigma^{-2N+6} \exp \left\{ -\frac{2N\bar{d}^2 - X + ZA^2}{2\sigma^2} \right\} I_0 \left( \frac{A}{\sigma^2} Y \right) \Big|_{\hat{\omega}_1 \hat{\alpha}_1 \hat{\omega}_2 \hat{\alpha}_2} \quad (30)$$

. If the standard deviation of the noise is known, the calculation is finished. The posterior probability for the amplitude of the sinusoid is given by Eq. (30).

If the standard deviation of the noise is not known, the sum and product rule from probability theory may be used to remove it from the problem. If a Jeffreys' prior is used the integral over the standard deviation,  $\sigma$ , may be obtained in closed form; but because of its complexity, it is essentially useless. Instead, an approximate solution will be given which is accurate to within the approximations already made. Notice that the argument of the Bessel function contains, among other things, a power spectrum as a function of  $\omega_1$ . Near the true values of the frequencies and decay-rate constants, the argument of the Bessel function will be large. Therefore, the Bessel function can be replaced by its large-argument approximation:

$$I_0(x) \approx \frac{e^x}{\sqrt{2\pi x}}. \quad (31)$$

Using this approximation and removing the standard deviation as a nuisance parameter, one obtains

$$P(A|D, I) \propto \left[ 1 - \frac{X + 2AY - ZA^2}{2N\bar{d}^2} \right]^{\frac{7-2N}{2}} \Big|_{\hat{\omega}_1 \hat{\alpha}_1 \hat{\omega}_2 \hat{\alpha}_2} \quad (32)$$

as the posterior probability-density for the amplitude independent of the standard deviation of the noise, where another term on the order of  $1/A$  was discarded.

## Example

To illustrate the use 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 real data were generated from

$$d_R(T_i) = 100 \cos(\omega_1 t_i) e^{-\alpha_1 t_i} + 200 \cos(\omega_2 t_i) e^{-\alpha_2 t_i} + e_i \quad (33)$$

where  $e_i$  represents a random Gaussian noise component of standard deviation one. The imaginary data were generated from the same equation except the sinusoids were shifted by

Figure 1: Amplitude Estimation

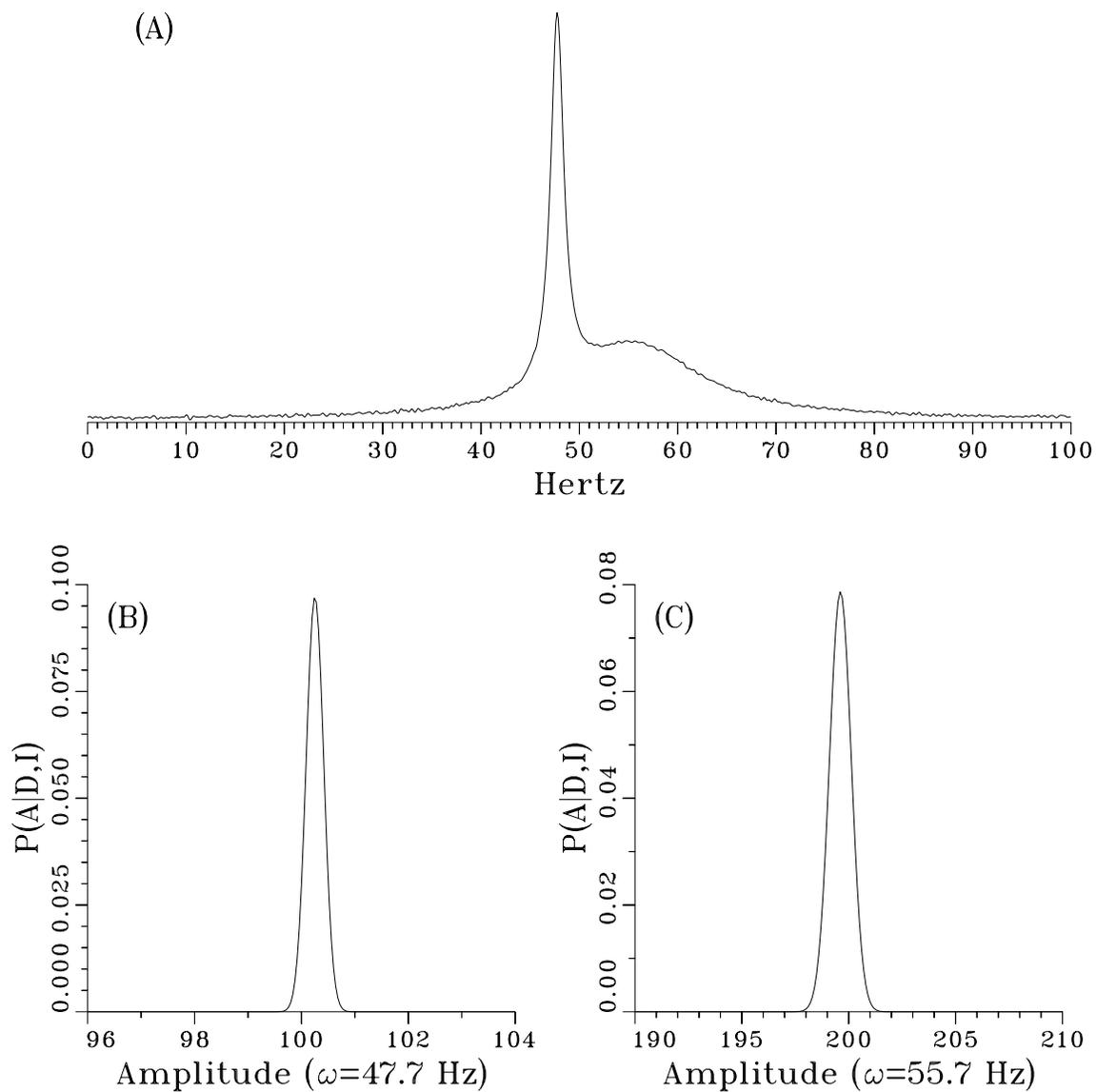


Fig. 1A is the absorption spectrum (the real part of the Fourier transform) of the computer simulated FID data. Traditional methods cannot estimate either the frequencies or the amplitudes of the sinusoids due to the overlap exhibited by the two NMR resonances. Panel B and C are the posterior probabilities for amplitudes of the sinusoids at frequency 47.7 Hz and 55.7 Hz respectively. These amplitudes are estimated to be  $100.24 \pm 0.2$  and  $200.6 \pm 0.5$ . The true values are 100 and 200.

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

$$\omega_1 = 47.7 \text{ Hz and } \alpha_1 = 1.6 \text{ Hz} \quad (34)$$

$$\omega_2 = 55.7 \text{ Hz and } \alpha_2 = 16 \text{ Hz.} \quad (35)$$

The peak amplitude to RMS signal-to-noise ratio is large; nonetheless, because of overlap, traditional methods would not be able to estimate the amplitudes. 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 estimated 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 by computing the posterior probability for the amplitudes using Eq. (32). The resulting probability-density functions are shown in Figs. 1B and C. Notice that both amplitudes have been well determined using Bayesian methods. For the sinusoid at frequency 47.7 Hertz, the amplitude is estimated to be  $100.24 \pm 0.2$ . The true value is 100. Panel C shows the posterior probability for the amplitude of the sinusoid at frequency 55.7 Hertz. This amplitude is estimated to be  $200.6 \pm 0.5$ . The true value is 200.

## Summary And Conclusions

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

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