Spectral Representation of 2D NMR Spectra by Hypercomplex Numbers

MARC A. DELSUC*

NIH Research Resource for Multinuclear NMR and Data Processing, Bowne Hall, Syracuse University, Syracuse, New York 13244-1200

Received June 29, 1987

This paper introduces a new spectral representation for phase-sensitive two-dimensional NMR experiments based on hypercomplex algebra. Some properties of this hypercomplex algebra are given. With this representation, it is shown that the Fourier transform and the phasing of phase-sensitive 2D NMR spectra can take simple expressions. Relationship of this representation with earlier proposed representation is considered.

Fourier transform nuclear magnetic resonance spectroscopy exhibits a quite unique feature among all Fourier transform spectroscopies: the phase of the signal is pertinent and not trivial; furthermore, the signal acquired is usually in a complex representation. This implies that the power spectrum representation is not suitable for FT NMR, and the complex representation is usually chosen for the spectrum. The notion of "phasing" a spectrum has been introduced, which consists in multiplying the complex spectrum by a given phase factor \( \exp(i\theta) \), in order to bring some interesting features of the signal in the real part of the spectrum.

The introduction of phase-sensitive two-dimensional NMR (1-4) has raised the need for a new type of spectral representation. A 2D NMR signal consists of a signal which is modulated along two independent time parameters, \( t_1 \) and \( t_2 \). By convention, \( t_2 \) corresponds to the usual time parameter of 1D NMR, whereas \( t_1 \) is an additional time parameter introduced in the excitation part of the experiment (5). The early attempts in 2D NMR (6, 7) used a complex representation for the acquired signal as well as a complex two-dimensional Fourier transform, leading to a mixed broad lineshape, the so-called "phase-twist" lineshape. Recently (1-4), it has been realized that the phase of the modulations in the two independent time domains could be separated, leading in certain cases to sharper lineshapes. However, this separation leads to a spectral representation where a point in the spectrum is not any longer described by a complex value, but rather by a set of two complex numbers, and a special Fourier transform must be used. The aim of this paper is to present a theoretical background for such a representation, as well as to provide useful relationships with the use of a hypercomplex algebra.

Hypercomplex algebras are linear algebras (8) which are presented as a generalization of complex-number algebra. Hypercomplex algebras have already been successfully...
used in gravitation theory (9, 10), in particle classification theory (11), and in NMR for the representation of composite pulses (12). Furthermore, the product operator decomposition (13), which has proven to be so useful in multipulse NMR, can be expressed as the direct product of hypercomplex algebras.

Let us introduce the four-dimensional algebra $H$ of hypercomplex numbers on the basis $1, i, j, k$, over the field of the real numbers,

$$z = z_1 + iz_2 + jz_3 + k z_4$$  \[1\]

with the following multiplication rules:

$$i^2 = j^2 = -1 \quad k^2 = 1$$

$$i \cdot j = j \cdot i = k \quad i \cdot k = k \cdot i = -j \quad j \cdot k = k \cdot j = -i.$$  \[2\]

Then the sum (denoted by $+$) and the product (denoted by $\cdot$) of two elements of $H$, $z$ and $z'$, are given by

$$z + z' = (z_1 + z'_1) + i(z_2 + z'_2) + j(z_3 + z'_3) + k(z_4 + z'_4)$$

$$z \cdot z' = z_1 z'_1 - z_2 z'_2 - z_3 z'_3 + z_4 z'_4 + i(z_1 z'_2 + z_2 z'_1 - z_3 z'_4 - z_4 z'_3)$$

$$+ j(z_1 z'_3 + z_3 z'_1 - z_2 z'_4 - z_4 z'_2) + k(z_1 z'_4 + z_4 z'_1 + z_2 z'_3 + z_3 z'_2).$$  \[3\]

With these definitions of sum and product, it can been shown that $H$ forms a linear associative and commutative algebra of order 4 on the field of the real numbers (8).

The numbers $1, i, j, k$ can be given a representation by a set of $4 \times 4$ matrices

$$1 = \begin{bmatrix} 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}, \quad i = \begin{bmatrix} 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 \\ 0 & 0 & 1 & 0 \end{bmatrix}$$

$$j = \begin{bmatrix} 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & -1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{bmatrix}, \quad k = \begin{bmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & -1 & 0 \\ 0 & -1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{bmatrix}. $$  \[4\]

These matrices can be seen as being the direct product of the matrices used for the representation of the complex numbers 1 and $i$. For instance $j = 1 \ast i$ and $k = i \ast i$ ( $\ast$ noting the direct product). It is also worth noting that the matrices $i, j,$ and $k$ are proportional to the operators $I_y, S_y,$ and $I_zS_y$ which appear in the product operator representation of a two-spin $I = S = \frac{1}{2}$ system.

For the $z = z_1 + iz_2 + jz_3 + k z_4$ element of $H$, one can define the complex part of $z$: $C_i(z)$ and $C_j(z)$ relative to $i$ and $j$, respectively, and the hyperimaginary part of $z$: $H_i(z)$ and $H_j(z)$ relative to $i$ and $j$, respectively, by the relations

$$C_i(z) = z_1 + jz_3$$

$$C_j(z) = z_1 + iz_2$$

$$H_i(z) = z_2 + jz_4$$

$$H_j(z) = z_3 + iz_4,$$  \[5\]
where \( C_i(z), C_j(z), H_i(z), \) and \( H_j(z) \) are isomorphic to complex numbers. Then the following relations can be found,

\[
z = C_i(z) + iH_i(z) = C_j(z) + jH_j(z),
\]

and for two elements of \( H, \) \( z \) and \( z' \),

\[
z \cdot z' = C_i \cdot C'_i - H_i \cdot H'_i + i(C_i \cdot H'_i + H_i \cdot C'_i),
\]

where \( C_i \) and \( H_i \) (respectively \( C'_i \) and \( H'_i \)) are the complex and hyperimaginary parts of \( z \) (respectively \( z' \)).

One can define the hyperconjugate \( z^+ \) of the hypercomplex \( z = z_1 + iz_2 + jz_3 + kz_4 \) by

\[
z^+ = z_1 - iz_2 - jz_3 + kz_4
\]

or

\[
z^+ = C^*_i(z) - iH^*_i(z) = C^*_j(z) - jH^*_j(z),
\]

where \( a^* \) note the complex conjugate of the complex number \( a \). Then the following relations hold:

\[
(z \cdot z')^+ = z^+ \cdot z'^+ = z \cdot z^+
\]

It can thus be seen that \( z \cdot z^+ \) is not a norm on \( H \).

We can now introduce the definition of a bicomplex number: a hypercomplex number \( z = z_1 + iz_2 + jz_3 + kz_4 \) is called bicomplex if the following relation applies:

\[
z_1z_4 - z_2z_3 = 0.
\]

If \( z \) is a bicomplex number, then the product

\[
z \cdot z^+ = z_1^2 + z_2^2 + z_3^2 + z_4^2 + 2k(z_1z_4 - z_2z_3)
\]

defines a norm for \( z \), so that an inverse of \( z \) can be found:

\[
z^{-1} = \frac{z^+}{z \cdot z^+}.
\]

It is easy to show that if \( z \) is bicomplex number, then a set of four real numbers can be found such that

\[
z = (a + ib) \cdot (c + jd).
\]

Thus \( z \) can be expressed as the (hypercomplex) product of two independent complex numbers. This set is obviously nonunique; however, one can define a unique representation of \( z \),

\[
z = R \exp(i\theta) \cdot \exp(j\psi)
\]

\[
= R(\cos \theta + i \sin \theta) \cdot (\cos \psi + j \sin \psi)
\]

\[
= R(\cos \theta \cos \psi + i \sin \theta \cos \psi + j \cos \theta \sin \psi + k \sin \theta \sin \psi),
\]

where \( R, \theta, \) and \( \psi \) are positive real numbers, \( \theta \) and \( \psi \) being defined modulo \( 2\pi \), and where the following definitions apply,

\[
R = \sqrt{a^2 + b^2} \cdot \sqrt{c^2 + d^2} = \sqrt{z \cdot z^+}
\]
Furthermore, \( \psi \) (or \( \theta \)) can always be restricted to the range \( 0 \cdots \pi \) because of the following relation:

\[
\exp(i\pi) \cdot \exp(j\pi) = 1.
\]  

[16]

For two bicomplex numbers \( z \) and \( z' \), \( z = R \exp(i\theta) \cdot \exp(j\psi) \) and \( z' = R' \exp(i\theta') \cdot \exp(j\psi') \), the product \( z \cdot z' \) is a bicomplex number and can be expressed by (see Appendix I)

\[
z \cdot z' = RR' \exp(i(\theta + \theta')) \cdot \exp(j(\psi + \psi'))
\]  

[17]

and the sum \( z + z' \) is a bicomplex number if and only if (see Appendix II)

\[
\theta = \theta' \pm k\pi \quad \text{or} \quad \psi = \psi' \pm k\pi.
\]  

[18]

In the set of the bicomplex numbers, the equation \( z^n = 1 \) possesses \( n^2 \) different roots (to be related with the \( n \) roots of the same equation on the complex plane). The \( n^2 \) roots are of the form

\[
z_{kl} = \exp\left(i \frac{k\pi}{n}\right) \cdot \exp\left(j \frac{l\pi}{n}\right)
\]  

[19]

with \( k = 0 \cdots 2n - 1 \), \( l = 0 \cdots n - 1 \), and \( k + 1 \) even. It must be noted that, because of relation [16], if \( z_{kl} \) is a root of 1, then the four numbers \( z_{k'l'} \) with \( k' \) element of \( \{k + n, k - n\} \) and \( l' \) element of \( \{l + n, l - n\} \) correspond to the same number \( z_{kl} \).

One can define the hypercomplex Fourier transform (hFT) of a hypercomplex function \( z(t_1, t_2) \) by the following:

\[
hFT(z(t_1, t_2)) = Z(\omega_1, \omega_2)
\]

\[
= \int_{-\infty}^{\infty} dt_1 \int_{-\infty}^{\infty} dt_2 z(t_1, t_2) \cdot \exp(i\omega_1 t_1) \cdot \exp(j\omega_2 t_2)
\]  

[20]

The digital hFT of the series \( z_{nm} \) is defined by:

\[
z_{kl} = \sum_{n=0}^{N-1} \sum_{m=0}^{M-1} z_{nm} \cdot \exp\left(2i\pi \frac{kn}{N}\right) \cdot \exp\left(2j\pi \frac{lm}{M}\right).
\]  

[21]

The hypercomplex numbers can be used to represent a phase-sensitive 2D NMR experiment. Each of the four independent real numbers can be used to define a hypercomplex number, corresponding to the so-called four quadrants (sometime noted RR, RI, OR, II), with (for instance), the \( t_1 \) direction corresponding to \( i \), and the \( t_2 \) direction to \( j \). The TPPI technique proposed by Marion and Wüthrich (2) can be represented in hypercomplex notation with the hyperimaginary relative to \( i (H_i) \) null.

With this representation, the hypercomplex Fourier transform proposed in Eq. [21]
corresponds formally to the one described by Keeler and Neuhaus (3) for the processing of phase-sensitive 2D experiments. The data format of a phase-sensitive 2D NMR experiment (two independent sets of complex data) corresponds to the representation of Eq. [6]. The Fourier transform is carried out using the multiplicative rules of Eq. [7]. During the transpose step, the representation is inverted from a decomposition in \( i \) to a decomposition in \( j \). The phasing of a 2D spectrum represented by a hypercomplex array consists simply of multiplying the spectrum by a bicomplex phase coefficient \( \exp(i\theta) \cdot \exp(j\psi) \), where \( \theta \) and \( \psi \) are the phase corrections in \( F_1 \) and \( F_2 \), which may be constant, or may have some linear relationships with the frequencies.

It is worth noting that if the function \( z(t_1, t_2) \) (or the time series \( z_{nm} \)) is bicomplex then the hypercomplex Fourier transform of it is also bicomplex. However, in the general case, a 2D NMR FID is not composed of bicomplex numbers. On the other hand, if, for a given 2D experiment, it can be shown that (i) the experiment can be phased in pure absorption mode, (ii) there is no first-order phase correction in one of the dimensions, and (iii) the noise contribution can be neglected, then the 2D experiment can be expressed as a sum of bicomplex signals, where relation [18] holds, and thus the 2D NMR experiment itself is bicomplex. The above conditions are easily fulfilled in a number of applications: condition (i) is fulfilled for most of the phase-sensitive experiments now used (DQF-COSY, NOESY, etc.) (13), and condition (ii) can usually be quite well approximated if the experimenter gives a small enough value to the initial time of \( t_{10} \) of the 2D experiment compared to the dwell time in \( t_1 \) (13).

ACKNOWLEDGMENTS

This work has been carried out in the NIH Research Resource for Multinuclear NMR and Data Processing, Bowne Hall, Syracuse University, Syracuse, New York, and I am particularly grateful to Dr. G. C. Levy for his constant support. I also thank A. Kumar for useful discussion and remarks. This work has been supported by NIH Grant RR-01317 and NATO.

APPENDIX I

Let two bicomplex numbers \( z = R \exp(i\theta) \cdot \exp(j\psi) \) and \( z' = R' \exp(i\theta') \cdot \exp(j\psi') \).

Then

\[
z \cdot z' = RR' \exp(i(\theta + \theta')) \cdot \exp(j(\psi + \psi'))
\]

\[
= RR' (\cos \theta + i \sin \theta) \cdot (\cos \theta' + i \sin \theta') \cdot (\cos \psi + j \sin \psi) \cdot (\cos \psi' + j \sin \psi')
\]

\[
= RR' (\cos \theta \cos \theta' - \sin \theta \sin \theta' + \cos \theta \sin \theta' + \cos \theta' \sin \theta)
\times (\cos \psi \cos \psi' - \sin \psi \sin \psi' + j \sin \psi \cos \psi' + \cos \psi \sin \psi')
\]

\[
= RR' \exp(i(\theta + \theta')) \cdot \exp(j(\psi + \psi')).
\]

APPENDIX II

Let two bicomplex numbers \( z = R \exp(i\theta) \cdot \exp(j\psi) \) and \( z' = R' \exp(i\theta') \cdot \exp(j\psi') \), and

\[
z + z' = A + iB + jC + kD.
\]
Then $z + z'$ is bicomplex if and only if

$$AD - BC = 0$$

$$\rightarrow (\cos \theta \cos \psi + \cos \theta' \cos \psi')$$

$$+ (\sin \theta \sin \psi + \sin \theta' \sin \psi')$$

$$- (\cos \theta \sin \psi + \cos \theta' \sin \psi')$$

$$+ (\sin \theta \cos \psi + \sin \theta' \cos \psi') = 0$$

$$\rightarrow \cos \theta \cos \psi \sin \theta' \sin \psi$$

$$+ \sin \theta \sin \psi \cos \theta' \cos \psi$$

$$- \cos \theta \sin \psi \sin \theta' \cos \psi$$

$$- \sin \theta \cos \psi \cos \theta' \sin \psi' = 0$$

$$\rightarrow \cos \theta \sin \theta' (\cos \psi \sin \psi' - \sin \psi \cos \psi')$$

$$+ \sin \theta \cos \theta' (\sin \psi \cos \psi' - \cos \psi \sin \psi') = 0$$

$$\rightarrow (\sin \theta \cos \theta' - \cos \theta \sin \theta') \sin(\psi - \psi') = 0$$

$$\rightarrow \sin(\theta - \theta') \sin(\psi - \psi') = 0$$

REFERENCES