Analysis of the Phases of Signals in Two-Dimensional NMR

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Introduction

An essential quality of NMR spectra is resolution. This can be obtained using strong and homogeneous fields in order to spread sharp signals over the largest possible frequency domain. Two-dimensional experiments allow one to further resolve signals in an additional protons or carbons dimension.

In order to fully exploit their potential in terms of resolution, NMR spectra should display signals with an absorption lineshape – as opposed to the dispersive or mixed-phase signals that are broader, as shown in Figures 1 and 2. This preference applied a strong evolutionary pressure on the developments of NMR. An early victim of this selection was the original two-pulses COSY sequence resulting to spectra where the diagonal signals and cross peaks have orthogonal phases in both spectral dimensions (See Figure 1(a)) (See emrstm0096). Because of the presence of extended dispersive tails making it difficult to observe cross peaks close to the diagonal, it was quickly replaced by the less sensitive but better-behaved double-quantum filtered experiments.

![Figure 1](image-url)

Figure 1. Comparison of the phases of cross peaks (top) and diagonal peaks (bottom) in COSY spectra. (a) Spectrum obtained using the two-pulse sequence with broad dispersive diagonal peaks. (b) Spectrum obtained using the three-pulse double-quantum filtered sequence. The diagonal multiplet is aliased from 1.02 to 4.02 ppm in the F1 dimension.

The J-resolved experiment is another important example of experiment suffering from a phase problem. In the absence of quadrature in the indirect dimension, it turned out to be very difficult to produce signals without the characteristic "twisted lineshape" (see emrstm0579.pub2, emrstm1362 and emrstm1485) It is only after a long series of incremental improvements that the nearly perfect, but somewhat less sensitive, PSYCHE 2D J-experiment was introduced.
We shall here consider the analysis of this type of “unphasable” spectrum to extract, correct and, in some cases, take advantage of the phases of signals. The method presented here is based on an automatic two-dimensional lineshape analysis of the individual signals of 2D spectra.

1.1 The Lorentzian lineshape

The normalized Fourier transform of a simple exponential decay results, as illustrated in Figure 3, to real ($R_e$) and imaginary ($I_m$) components with respectively absorptive ($A$) and dispersive ($D$) Lorentzian lineshapes:

\[
R_e = A = R \frac{R}{R^2 + 4\pi^2(v_0 - v)^2}
\]

\[
I_m = D = R \frac{2\pi(v_0 - v)}{R^2 + 4\pi^2(v_0 - v)^2}
\]

where $R$ is the relaxation rate and $v_0$ the resonance frequency of the considered spin. (emrstm0479)

The magnitude mode of the spectrum is defined as

\[
M = (Re^2 + Im^2)^{1/2}.
\]

The Figures 3(a) illustrate the obvious advantage of the absorption shape, that is a full linewidth at the half height (FWHH) of 1 Hz, compared to 1.7 Hz for the dispersive and magnitude
mode signals.

When the signal has a phase \( \varphi \), the spectrum results in a linear combination of the absorptive and dispersive lineshapes:

\[
Re = \cos(\varphi)A + \sin(\varphi)D, \tag{4}
\]

\[
Im = -\sin(\varphi)A + \cos(\varphi)D. \tag{5}
\]

**Figure 3.** Normalized Fourier transform of an exponential decay with a coefficient \( R = 1/\pi \) and an offset of 2 Hz. (a) Representation of the real (continuous line), imaginary (dash line) and magnitude (broad line) mode spectra. (b) Apparent phase \( \varphi \) of the spectrum. (c) Three-dimensional representation of the complex spectrum and (d) projection on the complex plane (DISPA representation).

These real and imaginary components can be plotted onto orthogonal dimensions as a three-dimensional complex spectrum shown in Figures 2(c) and 3(c). In this representation, one can make the fascinating observation that a complex Lorentzian produces a single-turn curl emerging from the origin with an angle corresponding to the phase of the signal. In the DISPA representation, the projection of the two components onto orthogonal axes shown Figures 3(d) and 4(d) forms a perfect circle with a unit diameter. When the phase is zero, it is centred at

\[
Re = 0.5, Im = 0 \tag{6}
\]

because Equations 1 and 2 can be combined to the equation of a circle:

\[
(A - 0.5)^2 + D^2 = 0.5^2. \tag{7}
\]

The one-dimensional features of the absorptive and dispersive Lorentzian such as the linewidth at half height, frequency at the top, bottom and zero-crossing positions - that are not always physically meaningful - are transformed into three-dimensional properties such as curl pitch, diameter and tilt, and apogee frequency, corresponding respectively to the signal’s relaxation rate,
amplitude, phase and frequency.

1.2 The apparent phase of a peak

When the phase of the peak is non-zero, as illustrated in Figure 4, one can observe that the angle between the Re-axis and the line running from the origin and cutting the circle in two equal halves corresponds to the phase of the signal. Finding the centres of circles in spectra may therefore represent a robust method to determine the phase of peaks. A more direct alternative consists in relying solely on the top point of the circle. This point is easily identified because it corresponds to a maximum in the magnitude mode spectrum. We shall call "apparent phase" the angle of the vector having the real and imaginary components of the spectrum as coordinates:

$$\phi(\nu) = \tan^{-1}\left(\frac{\text{Im}(\nu)}{\text{Re}(\nu)}\right).$$

(8)

It only has a physical meaning at the frequency of a peak. Indeed, Figures 3 and 4 show that this angle varies quite dramatically when moving away from the top of the peak in the magnitude mode. Over the spectral range of the FWHH of the magnitude signal, $\phi$ varies by $\pm 45$ degrees. It is a first indication that precise measurements of the phase of signals from noisy experimental spectra will be quite difficult.

**Figure 4.** Fourier transform of an exponential decay with a coefficient $R = 1/\pi$ and a phase of 30 deg. (a) Representation of the real (continuous line), imaginary (dash line) and magnitude (broad line) modes spectra. (b) Apparent phase $\phi$ of the spectrum. (c) Three-dimensional representation of the complex spectrum and (d) projection on the complex plane (DISPA representation).
We will see in the following how phases can be measured in 2D spectra and discuss the factors influencing the apparent phase of signals.

2 Two-dimensional experiments

In most 2D experiments, a quadrature scheme is used to separately detect the real and imaginary components of the indirectly detected signals. Two-dimensional spectra therefore have four components called quadrants corresponding to the four combinations of real and imaginary components in F1 and F2. The equation of the quadrant with real components in both dimensions is, by analogy to Equation 4:

\[
ReRe = 
\cos(\varphi_1) \cos(\varphi_2) A_1A_2 + 
\sin(\varphi_1) \cos(\varphi_2) D_1A_2 + 
\cos(\varphi_1) \sin(\varphi_2) A_1D_2 + 
\sin(\varphi_1) \sin(\varphi_2) D_1D_2.
\]

(9)

The four combinations of two-dimensional lineshapes are shown in Figure 5 together with a tore representation of the two independent phases.

Figure 5. Representation of two-dimensional Lorentzian lineshapes. (a) Contour plot of the four
combinations of absorptive (A) and dispersive (D) lineshapes in F1 and F2. (a) Graphical representation of the two independent phases of two-dimensional complex Lorentzian. The phases corresponding to the dotted path in (a) were drawn with a broad line in (b).

In standard J-resolved spectra, the absence of F1 quadrature means that only one angle determines the shape of the signals in both dimensions.

\[ Re = \cos(\varphi_2)(A_1A_2 + D_1D_2) + \sin(\varphi_2)(D_1A_2 + A_1D_2). \]  

(10)

The sum of the double absorptive and double dispersive signals causes the phase-twist lineshape observed in the insert of Figure 2a.

2.1 Measuring phases in 2D spectra

The apparent phases \( \phi_1 \) and \( \phi_2 \) of a two-dimensional peak can be determined either from the real or the imaginary components of the other dimension:

\[ \phi_1(u_1, u_2) = \tan^{-1}\left(\frac{\text{Im}Re}{\text{Re}Re}\right) = \tan^{-1}\left(\frac{\text{Im}im}{\text{Re}im}\right) \]  

(11)

\[ \phi_2(u_1, u_2) = \tan^{-1}\left(\frac{\text{Re}im}{\text{Re}Re}\right) = \tan^{-1}\left(\frac{\text{Im}im}{\text{Im}Re}\right). \]  

(12)

In practice, because the intensity of one pair of signals may be accidentally quite small, the corresponding estimate of the phase may have a large error. It is therefore more advisable to use the magnitude mode for the other dimension to combine the information content of the real and imaginary components.

The apparent phases should therefore be measured as:

\[ \phi_1(u_1, u_2) = \tan^{-1}\left(\frac{\text{Im}M}{\text{Re}M}\right) \]  

(13)

\[ \phi_2(u_1, u_2) = \tan^{-1}\left(\frac{\text{Im}M}{\text{Re}M}\right). \]  

(14)

Note that because the magnitude mode amplitudes can only be positive, the signs of the angles \( \phi_1 \) and \( \phi_2 \) are lost. They can nevertheless be recovered by testing which combination of angles matches best the signals intensities in the four quadrants.

2.2 Unphasable spectra

The phases of NMR signals are usually not controlled in the directly detected dimension.
This is due to a technical difficulty to align the phases of the detector and of the pulse generator. A manual or automatic phase correction is therefore necessary to display signals with their absorptive lineshape. In the indirect dimension, the spectra normally do not require phase corrections for properly written pulse sequences.

But some spectra, in particular the ones that cannot be recorded using quadrature detection, are not phasable. As mentioned in the Introduction, this may be either because the experiment produces different types of signals with orthogonal phases or, because they result in signals with the famous twisted-phase lineshape. In both cases spectra are usually displayed in the magnitude mode (see Equation 3) which effectively eliminates the phase dependence of the Equations 4 and 5. But the disadvantage is, again, broader signals.

3 Factors influencing lineshape

We discuss here the factors influencing the measurement of the signal phases.\(^8\)

3.1 Truncation and window functions

In experimental spectra, signals often do not show pure Lorentzian lineshapes. (see also emrstm0177) Field inhomogeneities and other experimental imperfections may significantly broaden and distort signals. The lineshape is also influenced by signal truncation or by the application of the window functions used to improve sensitivity or resolution.\(^9\)

The Figure 6 illustrates the effect of different window functions. Unsurprisingly, signal truncation causes oscillations about the circular trajectory of the signal while applying window function maintains a smooth trajectory.
Figure 6. Influence of commonly used window functions on the phase and lineshape of a singlet. (a) Exponential multiplication corresponding to a broadening of 1 Hz. (b) Multiplication with a Gaussian with a width at half height of 1 Hz. (c) Lorentzian to Gaussian transformation with LB = -0.8 and GM = 1.2. (d) Truncation after 0.5 second of acquisition and reduction of the truncation artefacts using (e) a $\cos$ or (f) a $\cos^2$ window function.

Except for the exponential multiplication all window function distort the DISPA circles. The idea to search for circles or make assumptions about the pitch of the curls (which is a function of the slope of the variation of the phase about the resonance) is not generally applicable unless the deformation caused by the window function is taken into account. But window functions have no influence on the position of the maximum of the magnitude mode spectrum, or the angle measured therein which is quite favourable.

3.2 Influence of nearby signals
NMR signals are rarely lone singlets. The influence of peaks near the one under scrutiny should therefore be studied in some details. The top row of the Figure 7 show that the presence of a signal with the same phase as a reference peak located at a distance four times their line widths causes an error in the phase measurement of 6 degrees. When the peaks have different phases, this can be much larger, even in the example in Figure 7(b) where the spacing is only 4.3 Hz. When bringing two peaks with equal phases closer, as in Figure 7(c), the phase error further increases until the splitting become unresolved as in Figure 7(d). The Figures 6(e,f) illustrate the cases of unresolved doublet and triplet structures to show that the imaginary component of the signal displays more distinct lineshape features than the dispersive components. This indicates that including the imaginary component in spectral analysis should be beneficial when trying to decipher unresolved features. This potential has been demonstrated by Marshall et al., and found applications in the analysis of quadrupolar nuclei, but has never been truly exploited in the analysis of high-resolution liquid-state NMR.
Figure 7. Influence of nearby signals on the phase of a peak of interest. (a) Two signals with the same phase and a distance of 4 Hz. (b) Same as (a) but with the phase of one of the signal shifted by 30 degrees. (c) Double doublet with J = 5 and 1 Hz. Unresolved (d) doublet and (e) triplet structures with a coupling of 0.6 Hz. All FWHH were of 1 Hz.

These examples demonstrate that the apparent phase of a peak is severely affected by nearby signals in a manner that is difficult to predict because it depends on their exact lineshapes and the relative phases of the pair of peaks considered. Attempts to correct these apparent phases using incremental corrections based on the expected impact of nearby signals were tested in the context of a phase-encoding of the carbon chemical shift in aliased HSQC spectra. But even if effective, this approach was not really satisfactory.12

4 Spectral decomposition and generation of corrected spectra

Given the sensitivity of the apparent phase of signals to the presence of nearby peaks we
decided to determine their phases using the brute force solution consisting in decomposing the spectra into a list of peaks.\textsuperscript{13} It determined the best fit of parameter-optimized simulated spectra with all the experimental data available. For quadrature experiments, the four quadrants were simultaneously compared to the synthetic spectra.

For the fitting procedure, the 2D cross peaks were assumed to be the direct product of the F1 and F2 lineshapes, an approximation which is neglecting the tilted nature of the effect of field inhomogeneities.\textsuperscript{14} The F1 and F2 lineshapes were assumed to be the convolution product of a Gaussian and a complex Lorentzian lineshape. The originality of our approach consisted in adding the phases in F1 and F2 as additional independent parameters of the peaks in contrast to usual fit based on Voigt shapes,\textsuperscript{15} that is the convolution product of a Gaussian with an absorptive Lorentzian. A standard $\chi^2$ best-fit procedure was used to measure the quality of the fit and drive the optimization of the peaks parameters. It took, as starting values for the optimization, the coordinates and the signal amplitude originating from a double magnitude-mode spectrum and the apparent phases obtained in the relevant quadrants.

Depending on the application (see below) the peaks were then sorted, phase corrected or eliminated according to their phases and synthetic spectra generated using the corrected parameters. Note that automatic discrimination of signals based on spectral properties is not a new idea. For example, symmetry properties of signals\textsuperscript{16} are commonly used as criterion to sort signals in peak-picking procedures, but we are not aware of application using peak phases as criterion.

4.1 Deviation from a pure Lorentzian lineshape

A careful look at the simulated spectrum of Figure 3(a) reveals that the Fourier transform of a pure exponential decay does not rigorously correspond to the equation of the Lorentzian shape. This is due to the circular nature of the frequency domain of FT-transformed FID’s. The tails of the signals, which may seem to be cut at the spectral boundaries, in fact appear at the other side of the spectrum and contribute to a baseline offset. In fact, the spectrum of Figure 2 should be considered as the sum of an infinite number of 20-Hz sections of the signals shape extending indefinitely in both directions. For the absorptive component, the effect is hardly visible and only consists in a small intensity offset. But the consequence for the dispersive shape is to cross horizontal axis not only on resonance at 2 Hz, as expected for a dispersive signal, but also at the “opposite side” of the
spectrum, that is at −8.0 Hz in the case illustrated in Figure 3(a). This effect may not be negligible when considering spectra with narrow spectral window, for example in case of signal aliasing. (See emrstm1187) When attempting to reconstruct experimental spectra with simulated spectra, it may therefore be preferable to consider the Fourier transform of the simulated exponential decays, rather than a pure Lorentzian, or to take this aliasing effect into account by adding to the main spectrum the expected tails of signals far enough from the resonance.

Note that an advantage of this circular property of FT-spectra is that the analysis of signals located near a spectral boundary does not need to be stopped at this limit. One can simply ignore the limit and find the rest of the aliased peaks at the opposite side of the spectrum.

5 Applications

5.1 Identification and elimination of the COSY diagonal

The analysis of the signals of two-pulses COSY spectra is particularly illustrative of the potential benefit of a phase discrimination of peaks. It is the prototype of a highly sensitive experiment that is disregarded only because of “phase problems”. (See emrstm0096)

The Figure 8 shows the diagonal signals of the CH$_3$ of an ethyl group. The triplet pattern is similar to that of 1D spectra but observed in both dimensions. The cross peak with the CH$_2$ also shows a triplet structure along F2, and quadruplet along F1, but because one of the active couplings shows an opposite-sign structure, the cross peak patterns is [+ 0 −] along F2 and a [+ + − −] along F1. (See emrstm0096)
Figure 8. Elimination of dispersive diagonal signals in COSY spectra. (a) Experimental spectrum obtained using the two-pulse sequence. (b) Simulated spectrum using fitted parameters. Simulations of the diagonal (c) and cross peak (d) signals with pure absorption lineshapes.

Note that spectral aliasing was used to reduce the acquisition time of this high-resolution spectrum bringing the diagonal and the cross peaks multiplets in close proximity. The real chemical shift of the methyl is 1.02 ppm (as observed in F2) ppm but the signal is aliased to 4.02 ppm in the F1 dimension.
Figure 9. Representation of the phases of COSY peaks. (a) Tore-plot of the phases of the peaks picked in the magnitude mode spectrum. One-dimensional representation of the (b) F1 and (c) F2 phases. The apparent phases of the peaks are identified by small dots on the core and in the “I” columns in (b,c). The values obtained after fitting the experimental spectrum to a model making no assumption about the signal’s phases are displayed using a broad dot and in the “F” columns. The corresponding spectrum is shown in Figure 8(b). The phases obtained after rounding the angles to -180, -90, 0, 90, 180 degrees used to discriminate cross and diagonal peaks are displayed at cardinal positions using open circles and in the “R” columns. The corresponding spectra are plot in Figure 8(c,d).

Figure 9 shows how the four combinations of positive/negative and absorption/dispersion peaks were discriminated. The phases measured directly at the position of the peaks, represented by small dots in Figure 9(a), were corrected by the fitting procedure to the values represented by broad dots. The values were rounded to correspond to one of the four types of peak located at the found at the four open-circles positions. The fact that some phases crossed the dotted line delimiting the two types of signals between A and F in Figure 9(b) shows that the apparent F1-phases alone would not have permitted a correct discrimination of the peaks while either the F1 or the F2 phases alone obtained from the spectral decomposition were totally reliable. Finally, the signals with 90/270 phases were used to generate the diagonal spectrum shown in Figure 8(c) after a 90-degree phase shift in both dimensions while the others were used to reconstruct the spectrum containing only the cross peaks in Figure 8(d).

5.2 Reconstruction of pure-phase J-Resolved spectra

The correction of the phase-twist lineshape of J-resolved spectra can be very effectively obtained using the ALPESTRE method which is determining the negative evolution times by backward linear prediction. But J-resolved spectra being the prototypical example of spectrum with “phase problems”, we wish to see if phase-sensitive spectral decomposition could also address the problem. To reproduce the phase twist, the simulations used for the best fit were the sum of a pairs of 2D lineshapes with orthogonal phases in both dimensions \( (AA + DD) \). Preliminary results shown in Figure 10(c,d) are encouraging even if not quite as good as the spectra obtained with PSYCHE 2D-J experiment shown in Figure 2(c).
Figure 10. Correction of the phase-twisted lineshape of J-resolved spectra as prior to spectral shearing. (a) Experimental spectrum displayed in the (a) magnitude and (b) phase-sensitive modes. (c) Simulated spectrum using fitted parameters with phase-twisted lineshapes. (d) Simulations using the same parameters but displaying pure absorption lineshapes with phases set to zero.

5.3 Phana-HSQC

Phana-HSQC (phase-encoding of the aliasing order of aliased spectra) is a heteronuclear experiment in which a short constant delay is introduced during the $t_1$ evolution time so that the phases of signals along the indirect dimension are not zero as in normal spectra, but are a function of the carbon chemical shift.\textsuperscript{12} This allows one to determine a phase-encoded chemical shift by measuring the $F_1$-phase of the peaks. Such a measurement of the carbon chemical shift in HSQC experiment is redundant and perfectly useless if the HSQC spectrum is recorded by fulfilling the Nyquist condition. But it is very useful to complement the missing chemical shift information caused by spectral aliasing. This phenomenon occurs when the spectral window in the indirect carbon dimension is set to a fraction of the full width – say 10 ppm instead of 160 ppm - as a mean to increase the spectral resolution in the indirect carbon dimension. (see emrstm1187)

In aliased spectra, the positions of the signals provide ambiguous chemical shifts in the indirect dimension, but they contain high-precision information because their scale is much finer. They function like the minute hand of a watch. Alone, they are usually not very useful, but they increase the precision of the information provided by another source of information, the phase-encoded chemical shifts, playing the role of the hour-hand of a watch. Just as the hour-hand, the phase-encoded chemical shifts do not require high-precision - only enough to determine, out of the different possible values, which is the correct one.

In the spectrum of Fig. 10, the carbon spectral window was set to $sW_c = 10$ ppm instead of the full 160 ppm. This improves the resolution of the spectrum by a factor 16. When recording the
HSQC at a carbon carrier frequency of 75 ppm, all signals appear aliased between 70 and 80 ppm. A signal observed at $\delta_\alpha = 75.196$ may therefore have a true chemical shift

$$\delta_{\text{real}} = \delta_\alpha + /- n_\alpha \cdot s \omega_\alpha,$$

(15)

where $n_\alpha$ is an integer in the range -7 to 8 corresponding to the 16 candidate carbon chemical shifts located in the -5 to 155 ppm range. In order to properly reconstruct the spectrum of Figure 11(d), phase-encoding of the chemical shifts was used to determine the correct value of $n_\alpha$. The maximal tolerated error on the phase measurement was $+/-$ 11.25 degrees. This corresponds to half the distance between two consecutive candidate chemical shifts.

**Figure 11.** Reconstruction of a high-resolution HSQC spectrum, using phase-encoding and spectral aliasing to determine precise carbon chemical shifts. (a) Experimental 10 ppm Phana-HSQC spectrum. (b) Simulated spectrum using the fitted parameters. The inserts indicate the aliasing order of the framed signals. (c) F1-corrected aliased spectrum obtained by setting the F1-phases to zero. (d) Reconstructed full-width high-resolution HSQC spectrum.

The peak parameters obtained using totally unrestricted phase and lineshape properties were not satisfactory. This can be observed in Figure 12(a) where some peaks are located in the wrong aliasing order lane. This problem could be corrected either by fixing the phases in the direct dimensions to zero as shown in Figure 12(b) (which requires phase correction of the spectrum in F2) or by forcing the signals identified as belonging to the same multiplet to share common lineshape parameters in the F1 dimension, as shown in Figure 12(c). The Figure 12(d) shows that
the typical phase error in the phase measurements in a standard non-coding HSQC is less than 10 degrees.

Figure 12. Comparison of the results of the determination of F1-phases from Phana-HSQC spectrum with (a) unrestricted optimization of all peak parameters, (b) with F2-phases set to zero, (c) imposing the phases and lineshape parameters in F1 to be equal for the peaks belonging to the same multiplets. (d) Same as (a) but without phase encoding. All phases should be zero.

5.4 Elimination of out-of-phase artefacts

Sometimes, NMR spectra present artefacts with a distinct phase property. A spectral decomposition measuring the phases of the peaks should therefore be able to identify and eliminate all the peaks failing to meet certain phase criteria. We applied this principle to identify and eliminate the out-of-phase second-order artefacts observed about the diagonal signals of homodecoupled DIAG spectra. These artefacts presenting a clear dispersive contribution in Figure 13(a) are caused by a lack of selectivity of the 20-ms Rsnob pulse used to refocus the coupling partners of the protons located at about 2.5 ppm. Filtering out all the signals with $|\phi_1| > 25$ degrees effectively eliminated all artefacts while retaining the true F1-decoupled diagonal signal shown in Figure 13(d). Note that the quality of the reconstructed spectrum is not fully satisfactory. The reconstructed multiplet is not as resolved along F2 as in the original spectrum of Figure 13(a).
Conclusion

We presented a proof of principle of the power of spectral decomposition including the determination of signals. If this type of analysis proves to be powerful and fast enough, it could result in a comeback of the robust and sensitive early versions of the COSY and J-resolved experiments.

More generally, the possibility to phase independently each signal in a spectrum has the potential to transform any spectrum diagnosed as "unphasable" into a perfectly exploitable source of information.

Established NMR experiments should also benefit from such an advanced peak-picking method to produce high-quality lists of peaks. They could contain lineshape properties including unresolved scalar information and statistical measurement of the confidence in the characterization of the signals. For example, two close lines could be listed as a doublet with a given coupling constant, or two accidentally nearby singlets. This type of information should be quite valuable at a post-processing analysis such as those involved in structure elucidation and identification of the components of mixtures. They should also facilitate the discrimination of solvent signals and diverse types of artefacts when they have distinct phases.
Related Articles

Emrstm0328, emrstm1181, emrstm0096, emrstm0579.pub2, emrstm1362, emrstm 0479, emrstm0177, emrstm1187

References

Further reading

emrhp0026, emrstm1158, emrstm0449, emrstm0107, emrstm1226, emrstm1384, emrstm1444, emrstm1472, emrstm0012, emrstm1226

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Biographical Sketch