Time-resolved subnatural-width spectroscopy

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Spectra that are narrower than the natural width of decaying states can be achieved by beginning the observation of signals at a fixed delay time after excitation rather than immediately afterward. These signals are weaker (and noisier) than the full, time-unresolved signals. Applications of this line-narrowing technique to precision spectroscopy are discussed, and the properties of the resulting signals are studied. Numerical simulations demonstrate that time-resolved line narrowing is highly desirable in a large number of cases.

In this Letter, certain general characteristics of spectroscopic signals narrowed to less than their natural widths are examined and discussed. The line-narrowing methods considered apply to optical (10^{15} Hz), microwave (10^{10} Hz), and nuclear (10^{20} Hz) spectroscopy. The most important characteristics common to these spectroscopies are the selection rules and the linewidths: the selection rules determine which levels may be connected by transitions, and linewidths dictate the ultimate precision of spectroscopic measurements. Sometimes the linewidths are determined by experimental conditions (Doppler, collision, apparatus size, recoil, local fields), and sometimes these effects can be reduced so that only the power broadening of the field inducing the transition determines the linewidths. Ultimately the width of every spectral line is limited by the finite time the system spends in one of the states of the transition: most commonly this time is the natural lifetime of an excited state, which therefore determines a natural width.[1]

Most precision spectroscopy is concerned with finding the center of a decay-broadened signal or the frequency of a decaying oscillation. Since these two types of signal are a Fourier-transform pair, measuring one yields results equivalent to measuring the other. Narrower signals (or longer decay times) can produce more-precise measurements.

In 1960, Hughes[2] suggested that the separated-oscillatory-fields method of Ramsey[3] could be applied to signals broadened by natural decay as well as to those broadened by apparatus limits. The basis of the method is the selection of those atoms (molecules, nuclei, etc.) that fail to decay in a few natural lifetimes, i.e., they survive in the transient state for a longer time. The time-evolving phase of the wave function ($iEt/\hbar$) is thus preserved because the atom remains in the state of energy E. This experimental technique produces narrower but significantly weaker signals.

Since 1960, there have been many experimental variations of this idea proposed and exploited,[4–13] all of which require discarding that part of the signal arriving shortly after the excitation of the state to be studied and measuring only the delayed and exponentially weakened signal. Experimental procedures must therefore be amenable to temporal resolution. The energy range spanned by these studies begins at the Lamb shift[6] at 10^9 Hz and reaches to Mössbauer intervals[8] at 10^{18} Hz. Significant linewidth reductions have resulted in substantial improvements in precision.

In this Letter, the basic features governing all such techniques are examined in both the absence and presence of noise, and conclusions about utility of time-resolved spectroscopy are presented. In general, there is nothing to be gained by discarding data as long as the information is understood. But spectroscopists *never* have complete information about their signal shapes, and therefore selective (unbiased) deletion of data can be of great help[14] and may even be necessary.

Consider a decaying oscillation (which may or may not be superposed on an exponential background) as shown in Fig. 1. The oscillation frequency ω_0 of the signal $S(t) = [1 + \alpha \cos(\omega_0 t + \phi)]e^{-\Gamma t}$ is not perfectly measurable because an experimenter has a limited time to make a measurement. This is reflected in the width Γ of the Lorentzian–Fourier transform (in the ω_0 region) $L(x) = 1/(1 + x^2)$, where $x = (\omega - \omega_0)/\Gamma$. The precision of measurement of ω_0 is limited by both Γ and the experimental noise: the experimental uncertainty can be

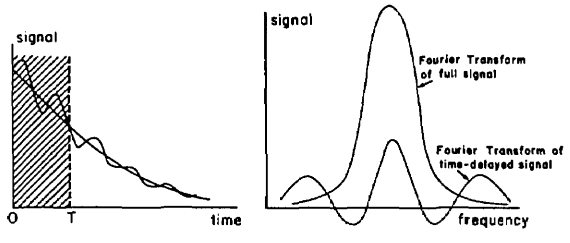

Fig. 1. An exponentially decaying oscillation and its Fourier transform. Note that beginning the transform at time T instead of at zero results in a narrower and weaker shape with oscillations (caused by the aperture).

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much smaller than Γ if the signal-to-noise ratio (S/N) is much larger than unity. On the other hand, Γ is the determining measure of the ultimate precision attainable. A smaller value of Γ (narrower Fourier transform) would result in a better measurement.

Suppose that all the data before time $t_0 \equiv T/\Gamma$ were ignored. The integral for the Fourier transform of $S(t)$ then would begin at t_0 instead of at zero, and the result would be (for $\phi = 0$)

$$F(x) = L(x)\, e^{-T}[\cos(xT) - x \sin(xT)], \quad (1a)$$

$$G(x) = L(x)\, e^{-T}[\sin(xT) + x \cos(xT)] \quad (1b)$$

for the real and imaginary parts. For T of order unity, the real part F has a maximum at $x = 0(\omega = \omega_0)$, a width of order Γ, and a height of order e^{-T}. For $x \ll 1$, T is Lorentzian, but at larger x it oscillates (see Fig. 1). As x increases from zero, $F(x)$ drops faster than the time-unresolved $L(x)$ because of the bracketed term, resulting in a narrower spectrum. Properties of the narrower and weaker time-resolved signals are shown in Fig. 2. Data characterized by this line shape can be computer fitted with high precision, in spite of the reduced amplitude and S/N, because the extra oscillations in the wings provide more information about the location of the central maximum than do the decaying tails of a Lorentzian transform. Furthermore, the effect of noise-hidden asymmetries that may shift the signal center is reduced because of the decreased width of the central maximum.

These line-narrowing effects occur only when the phase of the decaying signal is preserved by a measuring process such as heterodyning and do not occur if phase information is destroyed by a process such as measuring the power spectrum. This is easily seen by calculating the power spectrum $|F + iG|^2 = F^2 + G^2 = e^{-2T} L(x)$. The narrowing term [bracketed in Eq. (1)] is absent, and the spectrum has its full natural width. For $\phi \neq 0$, the algebra is slightly more complicated, but the conclusion is unchanged. Temporal resolution does not result in line narrowing when phase information is lost.

As a physical example of this procedure, consider analyzing radiation with a Fabry–Perot interferometer used as a spectrometer, followed by a photomultiplier or photographic film used as a detector. Such a system measures the power spectrum, and a shutter, introduced between the radiation source and the interferometer to perform time-delayed measurements, would not result in a narrower spectrum. The late radiation here does not have any narrower spectrum than the average of all the radiation. If the shutter were placed between the interferometer and the detector, however, the opposite conclusion would be reached. The radiation interferes with itself (heterodyne) in the Fabry–Perot interferometer, thereby extending the measurement interval, and the resulting spectrum is narrower. Lynch *et al.*[15] have demonstrated exactly this effect with Mössbauer apparatus. The signal from the early part of the decay is allowed to interfere with that from the later part of the decay, thus preserving the phase information required for line narrowing.

Although the foregoing discussion dealt with the spectrum of a decaying oscillation, finding the center of a decay-broadened spectral line presents the same

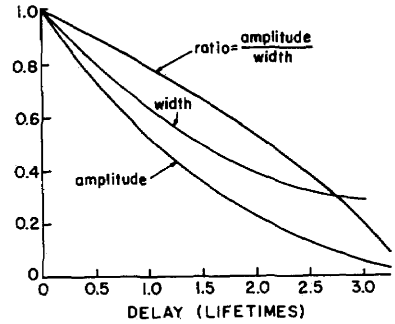

Fig. 2. Characteristics of the Fourier transform of time-delayed oscillations or of the spectrum of a time-delayed signal.

problem. For example, in time-resolved level-crossing spectroscopy,[4] the signal is narrowed in frequency (or applied field) by appropriate timing of the pulsed excitation and delayed observation. In fact, expansion of the general expression for time-resolved level-crossing signals [Eq. (4) of Ref. 4] in the limit of short excitation and observation intervals yields Eq. (1) above, as might be expected. In quantum-beat spectroscopy, the frequency of a decaying oscillation may be measured as levels are brought near their crossing point by external fields,[16] and this technique is exactly analogous to time-resolved level-crossing spectroscopy.

In order to study the possible experimental advantages of time-resolved spectroscopy, artificial data have been generated by adding $\sqrt{N}$ noise to signals of the form of Eq. (1). (It is assumed that any experiment has been improved to the point at which noise is dominated by counting statistics.) Symmetric and slightly asymmetric data with small, medium, and large S/N have been least-squares fitted with both symmetric and slightly (variable) asymmetric line shapes. Changing the noise spectrum from white noise to Gaussian had little effect on the results. Several thousand runs have been tabulated and appropriate statistical procedures performed. The principal conclusion is that spectroscopy experiments producing perfectly symmetrical data do not benefit from time-resolved narrowing techniques, but others do.

The numerical studies show that symmetric data fitted by a symmetric line shape produce a center frequency correct to within statistical error, with precision governed by S/N (number of counts). If the data and fitted line shape have a fixed asymmetry, the result is the same. The real danger arises when the data have some asymmetry that is not known [asymmetry in the spectrum is equivalent to a phase shift ϕ in the time-dependent signal $S(t)$]. In the presence or absence of a known asymmetry, *an unknown asymmetry causes large shifts of the center frequency, and a fitting program cannot detect the error*!

The data for the various time delays of Fig. 3 have been fitted, and the results are summarized in Fig. 4. If the asymmetry of the fitting program is fixed, the error can be much larger than the precision determined by the χ^2 of the fit, and a large hidden error results. On the other hand, if the program is allowed to vary the asymmetry, the high correlation between it and the

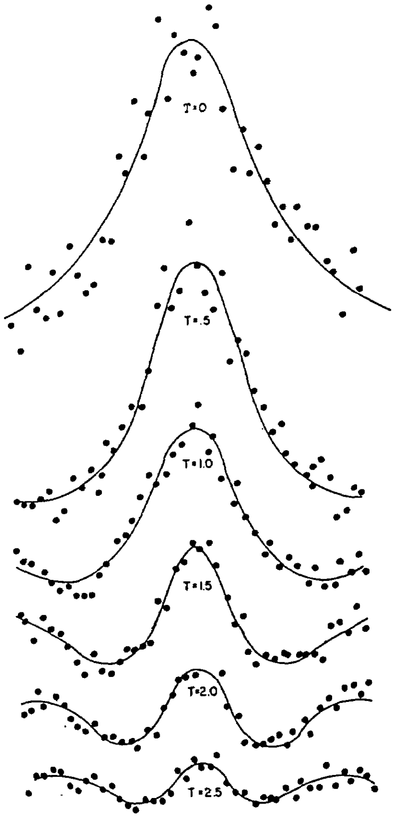

Fig. 3. A set of simulated data for several different time delays and their least-squares fits. The data have a small, noise-hidden asymmetry, but the fitted curves are symmetric.

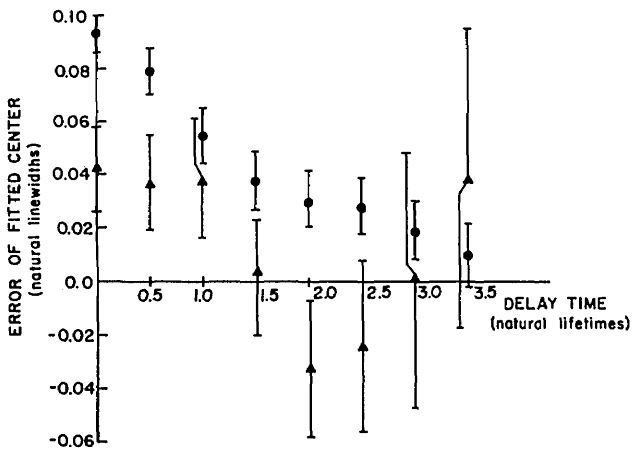

Fig. 4. The results of the fits in Fig. 3 (circles) show a residual error that decreases with increasing time delay. The bars are the standard error from 20 runs. Even though the S/N is lower at large T, the oscillations in the wings help locate the center. The results of fits with a variable asymmetry (triangles) having the wrong functional form also show residual error. The error bars are larger because of the high correlation of asymmetry and center frequency. The data had a small sloping baseline (about 0.5%) but were fitted with a signal having an asymmetry (odd term) that could be varied by the program.

center frequency results in a large uncertainty from the fitting procedure (Fig. 4), and in some cases it even fails to converge. Even with the variable asymmetry, there is significant remaining error if the functional form is not correct (e.g., sloping baseline instead of odd term). In both cases, time-delayed signal narrowing results in significant reduction of the error even though there is some (appropriate) loss of internal precision (Fig. 4).

In conclusion, the wide variety of line-narrowing methods, including the separated oscillating-fields technique, all share the common feature of waiting for a transient state to evolve for some fixed delay time. The resulting signals are narrower and weaker. The numerical studies reported here show that precision measurements benefit considerably from this time-resolved line narrowing, unless the experimenter has extraordinarily accurate knowledge of the signal shape. Since unknown systematic effects *usually* limit the ultimate accuracy of experiments, time-resolution techniques are *usually* desirable.

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