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Fourier Transform: A Tool to Measure Statistical Level Properties in Very Complex Spectra

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We show that the Fourier transform of very complex spectra gives a sound measurement of long-range statistical properties of levels even in cases of badly resolved, poorly correlated spectra. Examples of nuclear energy levels, highly excited acetylene vibrational levels, and singlet-triplet anticrossing spectra in methylglyoxal are displayed.

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Statistical properties of level spacings of quantum systems have formed a long-standing subject in nuclear physics since the pioneering work of Wigner¹ which laid down the basis of random matrix theory.² Recently they have deserved a lot of attention for several reasons. First, it has been realized that combining the results of all known nuclei [the so-called nuclear data ensemble (NDE)], rather than dealing with one nucleus at a time, opens the possibility of much more accurate and critical tests of theoretical predictions.³ Second, the statistical properties of eigenvalues in random matrix ensembles [usually the Gaussian orthogonal ensemble (GOE)] have been shown numerically to be the same as those of several quantum systems which are known to be chaotic in classical mechanics: various kinds of billiards⁴ and of coupled oscillators which may model molecular systems and which go classically from regular to chaotic regimes when energy or a coupling parameter increases.⁵ Finally, preliminary studies on experimental levels of atoms⁶ or molecules⁷ have given indications of Wigner statistics in these systems.

We will not try here to deal with the highly controversial nature of the relation (if any) between classical chaos and quantum level statistics.⁸ We estimate that level statistical properties are interesting to study in any case and we show that it is possible to obtain very significant measures even in "nonideal" situations, opening new avenues to analyze large amounts of "low-quality" data available especially in molecules. Indeed the statistical tests used in nuclear physics² (nearest-neighbor spacing for short-range, Σ^2 or Δ_3 tests for long-range properties) have been developed around the properties of the nuclear data available. The goal was to find the finest tests to characterize statistical properties of a relatively small (typically 50) set of consecutive levels. These levels came from high-quality data, with respect to noise, resolution, and purity (single J^π assignment), and made one confident that all levels having in common all good quantum numbers are known in a given energy range. Previous attempts to analyze the statistical properties of molecu-

lar energy levels have used the same kind of analysis: extracting from available data a "stick spectrum" (i.e., interpreted spectrum made of zero-width lines) and then applying the usual statistical tests to it. This was a very questionable procedure in these cases, however, because there are certainly a large number of levels lost either in the noise or in unresolved blends. Obviously this garbles the nearest-neighbor statistics, reducing the number of small spacings which is the most conspicuous difference between Poisson (random uncoupled levels) and Wigner (strongly coupled levels) statistics. Tests of long-range correlations are also corrupted.

The trick we use is to take the direct Fourier transform (FT) of the raw experimental data, to obtain a function $C(t)$, without any attempt to extract a stick spectrum. To interpret these experimental results we compute the average $\langle |C(t)|^2 \rangle$ for an ensemble of spectra, each composed of a sum of lines of given shape $L(f)$. The lines' random positions are described by the one- and two-level correlation functions² $R_1(f) = \rho$ (level density) and $R_2(f_1, f_2)$ (joint probability that there is a level at f_1 and another level at f_2), and their amplitude is the product of a stochastic component A_s , of unit mean, and a smooth envelope component $A_E(f)$. A_E can be a rectangle function in the case of a finite sweep over an otherwise constant-average-amplitude spectrum, or a Lorentzian or other more complex shapes in general cases. We suppose that the stochastic amplitude A_s is independent of the position of the line. The formal deviation will be given elsewhere.⁹ The result is sketched in Fig. 1(a). $\langle |C(t)|^2 \rangle$ contains two components: (i) A "fast component" which is the FT of the envelope $A_E(f)$. Its amplitude is proportional to N^2 , the square of the number of levels. It is proportional to $[\sin(Nt)/t]^2$ for a rectangle A_E , to a fast exponential decay for Lorentzian A_E , etc. (ii) A "slow component" which is the FT of the individual line shape $L(f)$. Its amplitude is proportional to N . Its shape is a slowly decaying exponential for a Lorentzian $L(f)$. If there are statistical correlations between level posi-

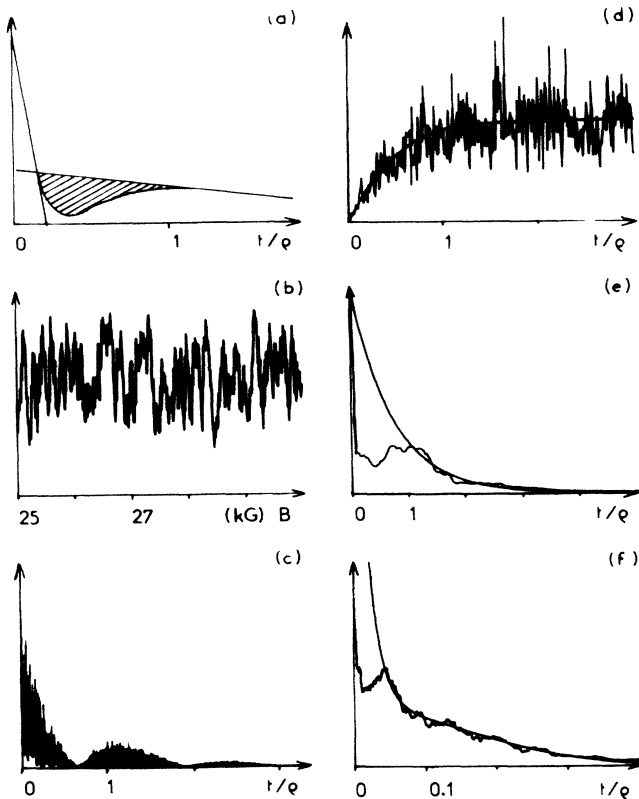


FIG. 1. (a) Theoretical averaged Fourier transform of a random spectrum. (b) A small part of a very complex spectrum: 0–80-kG anticrossing spectrum (Ref. 10) of the $N=0$, 137-cm^{-1} band of methylglyoxal (Ref. 11). Field scale converted to frequency scale with $g=2\text{ MHz/G}$. The widths of the individual lines $L(f)$ are also stochastic. (c) Effect of a nonrandom (hyperfine) doublet structure in the unsmoothed $|C(t)|$ (not squared) of spectrum (b). (d) FT (squared) of nuclear data ensemble compared to GOE theoretical predictions. (e) 30-points-smoothed FT of a SEP spectrum of acetylene (Ref. 7). (f) Expansion of the small-time part of 60-points-smoothed FT of spectrum (b).

tions, i.e., if $R_2(f_1, f_2)$ is not merely equal to $R_1(f_1)R_1(f_2) = \rho^2$, but given by

$$R_2(f_1, f_2) = \rho^2 [1 - Y_2(\rho f_1, \rho f_2)],$$

which defines the two-level cluster function Y_2 , the slow component is multiplied by $[1 - b_2(t/\rho)]/\langle A_s^2 \rangle$, where $\langle A_s^2 \rangle$ is of order unity since $\langle A_s \rangle = 1$, and b_2 is the FT of Y_2 . The presence of level correlation is thus evidenced by a “correlation hole” [shaded in Fig. 1(a)] which is a direct measure of b_2 . Notice the following:

(i) There is an obvious close relationship between this derivation and the double exponential decay theory of radiationless processes in intermediate molecules.¹² In this case, the molecular levels are observed as a result of the dilution of a single gate level which carries the oscillator strength into a set of dark

levels to which it is coupled. The present derivation is more general.

(ii) If the spectrum is not purely random, but contains a constant deterministic structure (e.g., fine, hyperfine, rotational structure), the slow component is multiplied by the FT of this structure. In other words, the individual line shape $L(f)$ may not be a single peak but, for example, a hyperfine-structure multiplet. Such a structure is clearly evidenced in the FT of the methylglyoxal anticrossing¹⁰ (ac) spectrum of Fig. 1(c), whereas it is completely unobservable in the original spectrum of Fig. 1(b): The arched structure comes from hyperfine doublets.

(iii) The ensemble average $\langle |C(t)|^2 \rangle$ is the smoothed function sketched in Fig. 1(a), but the slow component of an actual $|C(t)|^2$, resulting from the FT of a single spectrum, is 100% modulated, as seen in Fig. 1(c), whatever the two-point correlation function $R_2(f_1, f_2)$. This phenomenon is the exact analog of the well known laser speckle phenomenon, which is the consequence of the light making in the eye the space FT of a corrugated wall [the very complex spectrum of Fig. 1(b) mimics a vastly corrugated wall]. The 100% modulation occurs at time intervals of the order of the reciprocal of the width of the envelope A_E , which sets the fastest possible time variations. The lack of understanding of this point led Brumer and Shapiro¹³ to state erroneously that there is no difference between $|C(t)|^2$ coming from a chaotic (stadium) and a perfectly regular (two uncoupled anharmonic oscillators) system, because of the similar appearance of both the fast component and the speckle. In fact, the correlation hole is perfectly visible in their stadium results, and the peaks appearing at short times for their uncoupled oscillators are a consequence of the fact that this spectrum cannot be considered as random up to times of the order of the oscillator period. To recover the useful information, this “speckle noise” must be reduced by some kind of ensemble averaging (of several sequences of levels considered as equivalent) or time smoothing. The greater the number of levels available (up to thousands of levels in later examples), the better these procedures work.

(iv) The correlation hole $\approx 1 - b_2(t)$ is analytically known for the two opposite cases of completely random (Poisson) spectra, and of spectra coming from very strongly coupled systems, the Gaussian ensembles.² In the latter case $1 - b_2(t)$ goes from 0 for $t=0$ to 1 for reduced $t \approx 1$ (i.e., $t \approx \rho$). It is interesting to display some intermediate cases. First we consider the superposition of m independent GOE's. The correlation hole keeps the same shape, but it goes to 1 for reduced times $\approx 1/m$ instead of 1. It can thus be recovered with the same S/N ratio (after speckle averaging), if one has m times as many levels. This is

to be contrasted with the usual nearest-neighbor spacing test, for which the superposition of two GOE spectra already nearly destroys the minimum for zero spacing, and superposition of four GOE's is indistinguishable from the Poisson exponential law for every practical purpose. Second, for a more general intermediate case $1 - b_2(t)$ will not go to zero for $t=0$, but to a given value a , with a slope there of α . It is very interesting that there is a close relationship between these parameters and the Σ^2 test. $\Sigma^2(n)$ is the variance of the actual number of levels contained on a frequency interval which should contain on the average n . For Poisson statistics $\Sigma^2(n) = n$, which means that the actual number of levels is $n \pm \sqrt{n}$. For GOE statistics, it is known that the variance is greatly reduced, $\Sigma^2(n) \propto \log n$, a phenomenon known as long-range rigidity of the spectrum. We have shown⁹ that in any case one can write

$$\Sigma^2(n) = an + (\alpha/\pi^2)\log n + C + O(n^{-1}),$$

where a and α are the previously defined ordinate and slope at zero time of $1 - b_2(t)$, which thus measure respectively the Poisson and GOE components of an arbitrary distribution. This shows that $|C(t)|^2$ measures primarily long-range statistical properties of the level distribution. This is the reason why it is relatively insensitive to lack of resolution in the spectrum. Increasing the width of individual components makes the slow component decay faster; this garbles the measurement of long-time properties of $|C(t)|^2$ (the nearest-neighbor spacing information is contained in its asymptotic properties), but not of the short-time, most conspicuous parameters. This discussion is to be contrasted with the results of an autocorrelation measurement of the spectrum. For an ideal stick spectrum, this is as useful as the FT measurement since the autocorrelation, after an initial decrease corresponding to the correlation of every stick with itself, is equal to $1 - Y_2(f)$, giving directly the repulsion between neighboring levels. However, this is very sensitive to lack of resolution which fills in the $1 - Y_2(f)$ hole when the linewidth becomes of the order of the range of the repulsion. Furthermore, in the case of a superposition of m independent GOE's, $1 - Y_2(f)$ would be $1 - 1/m$ (instead of 0) at $f=0$, and its width would be increased m times, so that the repulsion hole rapidly disappears into the noise. This is analogous to the fast transition between Wigner and Poisson statistics in the nearest-neighbor test.

Finally we give in Fig. 1 three experimental examples. In all three cases the fast component is 1000 times off scale, and approximately one channel wide. Figure 1(d) shows the NDE³ compared to the GOE prediction. The speckle noise is not 100% because this is an ensemble average of data from 35 different nuclei. This is the first direct measurement of $b_2(t)$, of

nearly the same significance as other tests,³ showing the usefulness of this technique even for "ideal" spectra. Figure 1(e) is the 60-points-smoothed FT of the acetylene stimulated-emission pumping (SEP) spectrum of Abramson *et al.*⁷ This is a much more objective proof than the previous ones of the strong correlation of levels in this spectrum obtained at high vibrational energy (27900 cm^{-1}). Figure 1(f) is the 60-points-smoothed FT of the ac spectrum of methylglyoxal¹¹ given in Fig. 1(b). This looks much like the previous one, but the abscissa scale is dramatically different. The correlation hole has a width which is only $\frac{1}{30}$ of the density of states. The triplet levels which are monitored in this ac spectrum have only 3000 cm^{-1} of excitation energy and their coupling is very small. Part of this effect is due to this spectrum's being the superposition of independent spectra corresponding to two possible values of electron magnetic spin good quantum number and possibly to two values of two approximately good quantum numbers: molecular symmetry group label and symmetric top quantum number. This small coupling can be measured only because of the extreme sensitivity of our method when a great number (several thousands) of levels are available, even in a completely unresolved spectrum.

Penultimately, we make a comment on the hypothesis of the statistical independence of stochastic amplitude and position of the lines. This hypothesis is probably valid for strongly coupled systems, where the wave functions are completely mixed so that levels which carry oscillator strength are completely redistributed over all others. This is not valid in the low-coupling case when one measures primarily the statistical properties of only the levels which carry the oscillator strength. In intermediate cases one has a weighted average of the statistical properties of levels.

In conclusion, we have shown that the FT is a very sensitive and very robust (with respect to experimental "deficiencies") tool to measure statistical level correlations in complex spectra. It will be used to study the increase of coupling with increasing energy, hopefully up to dissociation limits, to shed light on the influence of vibrational coupling on the energy flow within molecules.

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