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Spurious spectral fluctuations due to missing levels

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We conduct a numerical experiment on a regular system which typically describes molecular vibrational modes. We find that randomly missing levels do not affect spectral properties significantly, but the effect of levels missing systematically in quantum number space can distort the statistics considerably, yielding results apparently consistent with the Berry-Robnik prediction for mixed systems. This observation underscores the important point that misleading interpretation of data is possible, and is of particular relevance in an experimental context.

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One important aspect of dynamical studies in recent times has been to explore the effects of the underlying classical mechanics on quantum stationary state properties. There is accumulating evidence that the energy eigenvalue statistics of quantum systems show universal fluctuation patterns determined by the nature of their classical analogs [1,2]. The simplest spectral characteristic is the nearest-neighbor spacing distribution $P(s)$, defined such that $P(s)ds$ is the probability of finding consecutive levels within distance s and $s+ds$. For generic integrable systems where the contours in action space are curved, it has been shown that $P(s)$ is Poisson distributed, i.e., the spectrum is characterized by level clustering [3]. Chaotic systems, on the other hand, display level repulsion and are well approximated by the Wigner distribution $P(s)=(\pi s/2)\exp(-\pi s^2/4)$, a result known to be true for a Gaussian orthogonal ensemble (GOE) of random matrices [4]. Higher-order correlations, which prove to be more reliable, are also used in analysis of spectra. For instance, the Δ_3 statistic is a commonly calculated quantity [5], and is given as the averaged least-squares deviation from the best straight line fitting a given substretch of levels in units of mean level spacing. For an uncorrelated Poisson spectrum $\Delta_3(L)$ is equal to $L/15$ while for the GOE it is equal to $\ln(L)/\pi^2-0.007$ for large L.

It is, of course, of utmost interest to discover these correlation patterns in experimental spectra of atomic and molecular systems. Consequently, much experimental data have been examined statistically, and inferences drawn about the nature of the underlying classical phase space [6]. Now analysis of experiments crucially hinges on the completeness and purity of the data set. But it is highly probable, if not an inescapable reality, that levels will be missing in real spectroscopic measurements. We then have to reckon with incomplete level sequences, and so it is of considerable importance to know theoretically how missing levels affect statistical properties.

The effect of *randomly* missing levels on GOE statistics is known to be not very significant [7]: for asymptotically long sequences, random missing levels push the GOE result a little towards the Poisson. In this paper we deal with the case of levels missing, both randomly and systematically in quantum number (action) space, in a regular system whose complete energy sequences exhibit Poisson statistics. We find that the effect of randomly missing levels is not drastic, but levels missing systematically in quantum number space (which may be more likely in certain experimental realizations, due to selection rules) influence statistical properties considerably and the resulting spectral patterns can easily be mistaken as coming from an underlying mixed classical system. This strongly suggests the need for caution in interpreting statistical tests. We demonstrate our point by numerical experiments on the model molecular Hamiltonian described below.

The classical microscopic description of the vibrational motion of a molecule is through a potential energy function. In suitable normal or local mode coordinates q, the vibrational part of the potential typically has a polynomial form [8]

$$V=\tfrac{1}{2}\sum_i \omega_i^2 q_i^2+\sum_i k_{ijk}q_iq_jq_k+\cdots \tag{1}$$

and the total classical Hamiltonian is

$$H=\sum_i p_i^2/2m+V\ , \tag{2}$$

where p are the respective conjugate momenta and N is the number of degrees of freedom. The main term in V is the harmonic part and the higher-order coefficients k_{ijk} are generically small. Since the essential complexities are already apparent for two degrees of freedom, many studies have been made on two-dimensional perturbed oscillator models such as [9]

$$H=\tfrac{1}{2}(p_x^2+p_y^2)+\omega_x^2x^2+\omega_y^2y^2+a(x^3+y^3)+bx^2y^3+cx^2y^2\ . \tag{3}$$

This Hamiltonian may be considered appropriate to model a two-mode molecule, for example, a nonbending triatomic molecule with x and y the symmetric and asymmetric stretch coordinates, and p_x and p_y the respective conjugate momenta. The frequencies of the two modes are ω_x and ω_y, the perturbation parameter a is the non-

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linearity, and b and c represent mode-mode coupling; these are the essential features in a realistic molecular system. We use the above system for our studies, in the range of parameters and energies for which it is classically regular [9].

Classical perturbation theory for the Hamiltonian in Eq. (3), using Lie transforms [10] up to second order, gives the normal form [9]

$$\begin{aligned}H=&\omega_1 I_1+\omega_2 I_2+\{c/\omega_1\omega_2\}I_1 I_2+I_1^2\{-15a^2/4\omega_1^4\}+I_2^2\{-15a^2/4\omega_2^4\}\\&+I_1^2 I_2\{c^2/2\omega_1^2\omega_2[1/(2\omega_1^2-2\omega_2^2)-1/\omega_2^2]\}\\&+I_2^2 I_1\{-c^2/2\omega_2^2\omega_1[1/\omega_1^2+1/(2\omega_1^2-2\omega_2^2)]+15ab/2\omega_2\omega_1^4-81ab/32\omega_1\omega_2^2(9\omega_2^2-4\omega_1^2)\}\\&\quad+I_1^2 I_2^2 b^2\{-27/16\omega_1^2\omega_2^2(9\omega_2^2-4\omega_1^2)-15/4\omega_2^4\omega_1^2-27/16\omega_1^2\omega_2^2(\omega_2^2-4\omega_1^2)\}\\&\quad+I_1 I_2^3 b^2\{9/(\omega_2^2-4\omega_1^2)-2/(9\omega_2^2-4\omega_1^2)\}/2\omega_1\omega_2^3\ .\end{aligned}\tag{4}$$

For quantum levels, using Einstein-Brillouin-Keller (EBK) quantization rules [11], we make the correspondence $I_1=n+\frac{1}{2}$ and $I_2=m+\frac{1}{2}$, for a level with quantum numbers m and n, in the above expression. This procedure yields very accurate results as comparative studies with exact results bear out [9]. We first generate sets of energy levels by scanning the quantum number space $\{m,n\}$. After these sequences are ordered they are unfolded via a polynomial unfolding function. Complete energy sets of this system show Poisson statistics [see Fig. 1 for nearest-neighbor spacing distribution (NNSD) and Fig. 2 for Δ_3 statistic], as is consistent with the regularity of the underlying classical dynamics. A total of 600 levels has been used in the analysis, keeping in mind that the typical numbers involved in experiments are usually of this order. Note that we have used the smooth approximation to the exact NNSD $[P(s)=(1/N)\sum_i\delta(s-s_i)$ where the total number of levels is $N+1]$ by expanding $P(s)$ in a complete set of basis functions [12]. This prevents errors and manipulations entering through the arbitrariness of the bin size, as is common in the histogram representation.

First we treat the case of levels missing randomly. We calculate the NNSD and the Δ_3 statistic for suitably unfolded level sequences with some fraction f_m of random missing levels. Figures 3 and 4 display the results of NNSD and Δ_3, respectively, for a representative case of $f_m=0.2$. Clearly the results are close to that for complete sequences, namely, Poisson. Note that the histogram representation of the spacing distribution would have shown excellent agreement with Poisson. In order to get a more quantitative idea, we have fitted the data to predictions for mixed systems. The NNSD for a mixed system was given by Berry and Robnik to be [13]

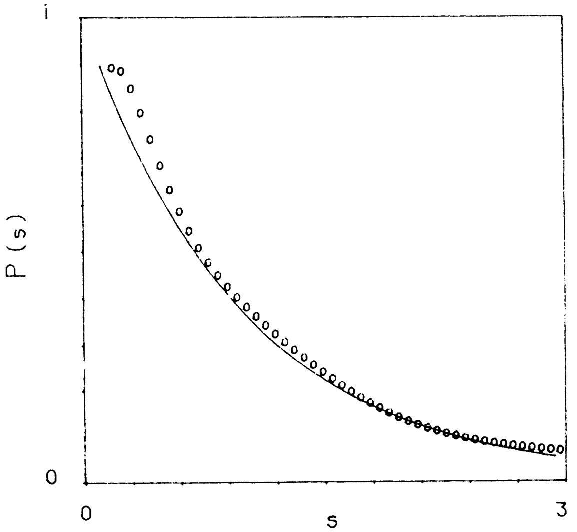

FIG. 1. The open circles denote the NNSD $[P(s)]$ for the unfolded levels of the system given in Eq. (3), with parameter values $\omega_x=1.9046$, $\omega_y=6.765$, $a=0.08$, $b=0.1$, $c=0.1$. The continuous curve is the Poisson distribution (e^{-s}). We take 600 levels in the stretch 200–800.

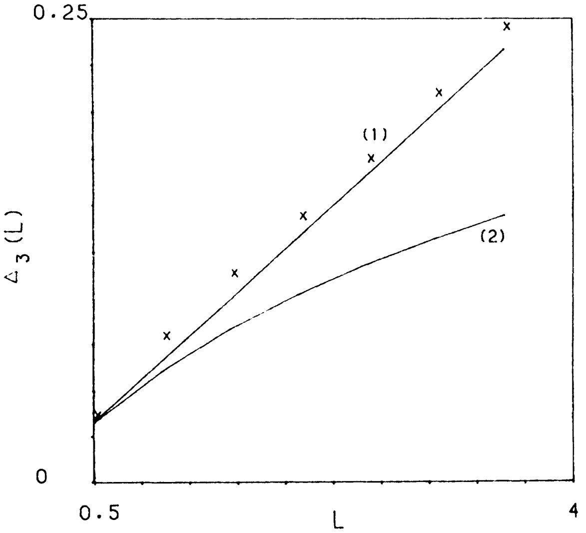

FIG. 2. The spectral rigidity Δ_3 for the system in Fig. 1 $(\times\times\times)$ in comparison with (1) the Poisson prediction $(L/15)$, (2) GOE result.

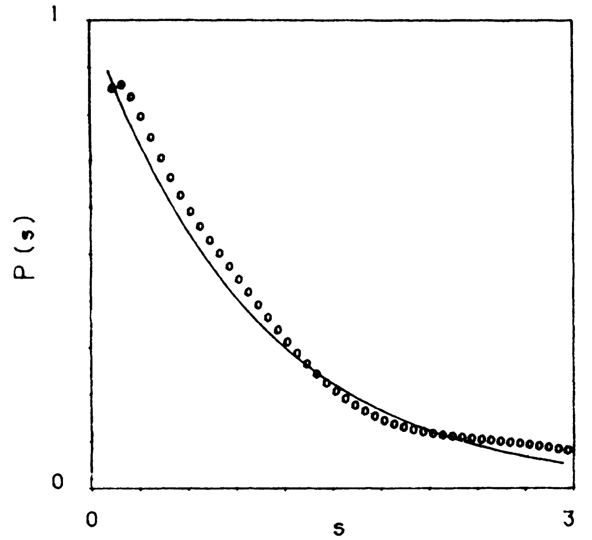

FIG. 3. As in Fig. 1 with randomly missing levels. The fraction f_m is 0.2. The continuous curve is the best fit Berry-Robnik distribution [Eq. (5)] with $\nu=0.93$.

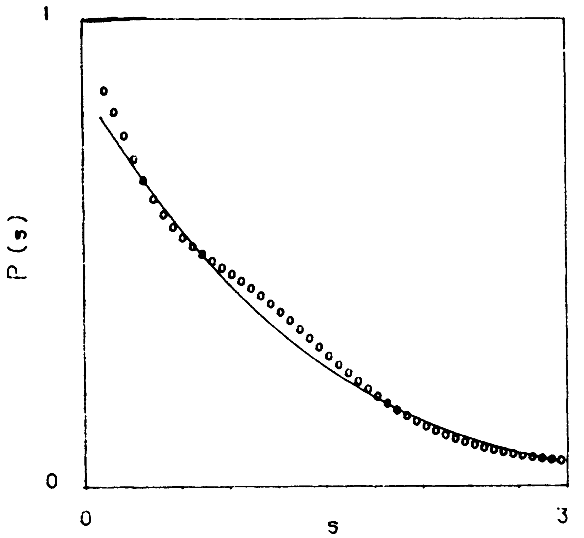

FIG. 5. As in Fig. 1 with levels missing systematically (see text for details). The continuous curve is the best fit Berry-Robnik distribution [Eq. (5)] with $\nu=0.62$.

$$P(s)=\nu^2\exp(-\nu s)\mathrm{erfc}(\tfrac{1}{2}\sqrt{\pi}\bar{\nu}s)+(2\nu\bar{\nu}+\pi\bar{\nu}^3s^2)\exp(-\nu s-\tfrac{1}{4}\pi\bar{\nu}^2s^2) \quad (5)$$

with $\nu+\bar{\nu}=1$, and ν parametrizing the fraction of phase space supporting regular dynamics. The expression for spectral rigidity analogous to the Berry-Robnik distribution for the NNSD is

$$\Delta_3(L;\nu)=\Delta_3^{\mathrm{Poisson}}(\nu L)+\Delta_3^{\mathrm{GOE}}(\bar{\nu}L)\ . \quad (6)$$

In Fig. 3, the continuous curve is the best fit of the data (marked as open circles) to Eq. (5). In Fig. 4, curve 1 is the Poisson prediction, curve 2 is the GOE prediction, and curve 3 is the closest fit of our data (marked as ×) to Eq. (6). In both cases, the degree of regularity is a fitting parameter, ν, which is large, indicating that the spurious "level repulsion" induced by randomly missing levels is not much.

Levels missing systematically have experimental relevance as well. Observation of a quantum state depends on the intensity of the spectral line which is determined by the probability of the transition which gives rise to it [8]. For instance, for a molecule whose vibrational wave functions are products of harmonic oscillator functions [e.g. Eq. (3)], the only vibrational transitions which occur with the emission or absorption of radiation are

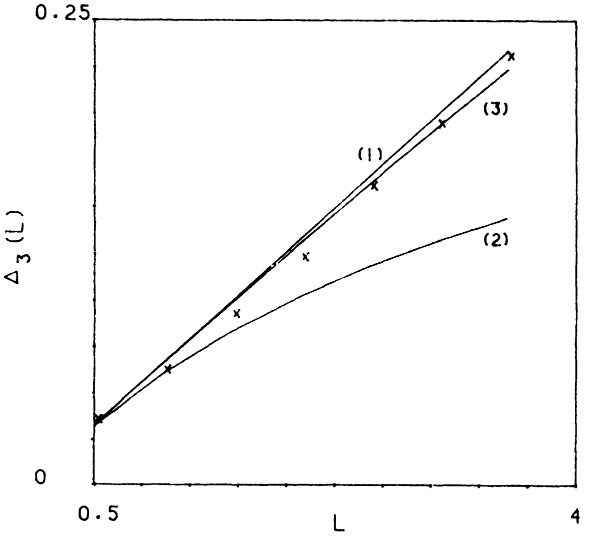

FIG. 4. The spectral rigidity Δ_3 for the system in Fig. 3 (×××) in comparison with (1) the Poisson prediction ($L/15$), (2) GOE, and (3) the best fit rigidity of Eq. (6) with $\nu=0.65$.

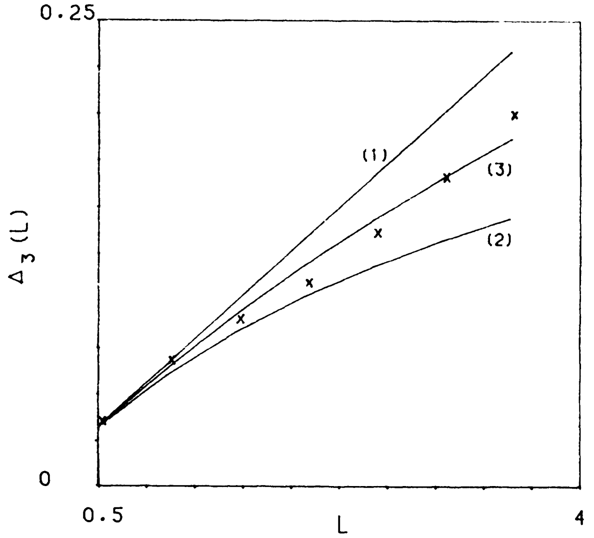

FIG. 6. The spectral rigidity Δ_3 for the system in Fig. 5 (×××) in comparison with (1) the Poisson prediction ($L/15$), (2) GOE, and (3) the best fit rigidity of Eq. (6) with $\nu=0.30$.

those in which only one quantum number changes, and by one quantum only (assuming that only linear terms in the expansion of the electric moment are important). Such selection rules demand that we take into consideration the possibility of levels missing in a systematic manner in action space in experimentally observed spectral sequences.

So, now we treat the case of levels missing systematically in quantum number space. Figures 5 and 6 show an illustrative example where every alternate quantum number is taken, that is, the quantum number space is scanned in steps of two. We calculate the NNSD and Δ_3 statistic for this case (Figs. 5 and 6, respectively) and as before compare our results with the best fit to Eqs. (5) and (6). It is evident that the fluctuations are now similar to that of mixed systems. While the rigidity is clearly close to the GOE result, a "shoulder" develops in the spacing distribution, $P(s)$ (again, a histogram representation of NNSD would have shown an excellent fit). The values of ν are small, apparently indicating the presence of a large chaotic subspace.

Our study highlights the inadequacy of examining NNSD alone (see also Ref. [14]) which can be misleading. However, probes of long-range correlations such as Δ_3 are more discerning and hence reliable. For instance, Figs. 2, 4, and 6 show a clear transition from Poisson (for a complete sequence) towards the GOE result whereas the effect on the NNSD is much less pronounced.

In summary, missing levels induce spurious fluctuations that may be interpreted as arising from an underlying mixed system. Interestingly, levels missing systematically (which is probable in many spectroscopic realizations) affect spectral statistics much more than randomly missing ones. This is evident in the smaller values of ν indicating a larger degree of apparent irregularity. This suggests a warning for the interpretation of experimental data. For instance, there are systems that are expected to be regular but surprisingly show chaoticity in the quantal spectra [15]. Such contradictions may partly be explainable in terms of arguments presented in this paper.

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[1] O. Bohigas and M.-J. Giannoni, in *Quantum Chaos and Statistical Nuclear Physics,* edited by T. H. Seligman and H. Nishioka, Lecture Notes in Physics Vol. 263 (Springer-Verlag, Berlin, 1986).
[2] B. Eckhardt, Phys. Rep. **163**, 207 (1988).
[3] M. V. Berry and M. V. Tabor, Proc. R. Soc. London, Ser. A **356**, 375 (1977).
[4] O. Bohigas, M.-J. Giannoni, and C. Schmit, Phys. Rev. Lett. **52**, 1 (1984).
[5] F. J. Dyson and M. L. Mehta, J. Math. Phys. **4**, 701 (1963).
[6] R. U. Haq, A. Pandey, and O. Bohigas, Phys. Rev. Lett. **48**, 1086 (1982); O. Bohigas, R. U. Haq, and A. Pandey, *ibid.* **54**, 1645 (1985); N. Rosenzweig and C. E. Porter, Phys. Rev. **120**, 1698 (1960); H. S. Camarda and P. D. Georgopoulos, Phys. Rev. Lett. **53**, 492 (1983); M. Lombardi, P. Labasti, M. C. Bordas, and M. Broyer, J. Chem. Phys. **89**, 3479 (1988); T. Zimmermann, H. Koppel, L. S. Cederbaum, G. Persch, and W. Demtroder, Phys. Rev. Lett. **61**, 3 (1988); E. Haller, H. Koppel, and L. S. Cederbaum, Chem. Phys. Lett. **101**, 215 (1983); A. Ferretti, G. Moruzzi, and N. K. Rahman, Phys. Rev. A **36**, 3736 (1987).
[7] S. Mukamel, J. Sue, and A. Pandey, Chem. Phys. Lett. **105**, 134 (1984); J. B. French, V. K. B. Kota, A. Pandey, and S. Tomsovic, Ann. Phys. (N.Y.) 181, 198 (1988).
[8] E. B. Wilson, J. C. Decius, and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955); C. H. Townes and A. I. Schalow, *Microwave Spectroscopy* (McGraw-Hill, New York, 1955).
[9] S. Sinha, Ph.D. thesis, Bombay University, 1989 (unpublished), and references therein.
[10] A. J. Lichtenberg and M. A. Lieberman, *Regular and Stochastic Motion* (Springer-Verlag, New York, 1983).
[11] I. C. Percival, Adv. Chem. Phys. **36**, 1 (1977); J. Phys. B **6**, L229 (1974).
[12] A. Honig and D. Wintgen, Phys. Rev. A **39**, 5642 (1989).
[13] M. V. Berry and M. Robnik, J. Phys. A **17**, 2414 (1984).
[14] S. Sinha and R. Ramaswamy, J. Phys. B **22**, 2985 (1989).
[15] H. A. Weidenmuller, Nucl. Phys. A **520**, 509c (1990).