

Energy-level statistics for a relaxation Hamiltonian

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We report a numerical computation of the energy-level spacing distribution, the spectral rigidity, and the transition-amplitude distribution for an ensemble of Hamiltonians with a single "bright" state interacting with a manifold of "bath" states. The bath states are assumed to be part of a regular spectrum so that the initial states have Poisson statistics. Despite very strong average coupling of all bath states to the bright state (which may represent coupling to another electronic surface), statistical properties of the final spectrum are more like those of the initial bath distribution than those of the Gaussian orthogonal ensemble distribution expected for an irregular quantum spectrum. The level spacings show level repulsion, but with the nonlinear threshold behavior $P(s) \sim s^{0.625}$.

The study of the statistical properties of energy levels has a long history, most notably in nuclear physics.¹ In the last few years, this study has received renewed attention, due to a conjectured relationship between the statistical properties of energy levels and the concepts of regular and irregular quantum states introduced by Percival.² A regular quantum state is one whose Wigner function³ is restricted to a small part of the energy shell in phase space. Such states are perturbed versions of the eigenstates of an integrable Hamiltonian. Berry and Tabor⁴ have shown that the eigenvalues of a generic separable Hamiltonian form a Poisson sequence so that level spacings are distributed according to a negative exponential distribution. This same distribution is expected for the more general case of an integrable Hamiltonian if quantum-mechanical tunneling splittings can be neglected. An irregular quantum state is one which is strongly delocalized in phase space and thus strongly mixed in the basis set of any integrable Hamiltonian. Wave functions of irregular states are conjectured to be random functions of coordinates⁵ with the Wigner function spread over the whole energy shell—like a microcanonical ensemble, but with nodes.⁶ Pechukas⁷ has demonstrated that, in the limit $\hbar \rightarrow 0$, irregular eigenstates should have the same energy-level spacing distribution as the Gaussian orthogonal ensemble (GOE), whose form is known and is closely approximated by the Wigner surmise, $P(s) = (\pi s/2D^2) \exp(-\pi s^2/4D^2)$. In the GOE model, the many large off-diagonal matrix elements cause the level repulsion of the Wigner distribution, as well as spectral rigidity, traditionally measured by Δ_3 . In diagonalizations of large, sparse matrices, the average size of off-diagonal matrix elements has been related to level repulsion, and the maximum size to spectral rigidity.⁸ In the regular case, strong approximate selection rules mean that most off-diagonal matrix elements are exponentially damped, so that the eigenspectra show neither level repulsion nor rigidity. Berry has shown that, in the semiclassical limit (classically small energy ranges containing many levels), the Poisson and GOE limits of spectral rigidity apply to spectra of classical Hamiltonians which are either integrable, or chaotic (all closed orbits isolated).⁹ Statistical tests

must be applied to each symmetry class separately so that energy separations are not confused by the spacing relationship between noninteracting classes. If independent GOE distributions are superimposed, the level spacing distribution rapidly approaches the negative exponential distribution of a Poisson process. Thus the existence of just one conserved action other than total energy, causes a near-Poisson spacing distribution, even if the wave functions are irregular in the other degrees of freedom.

In this paper we report on the numerical study of the statistical properties of a class of Hamiltonians where all basis states interact only through one coupling state. This type of Hamiltonian arises whenever one treats "relaxation" of a prepared, nonstationary state (bright state) into a dense manifold of "heat-bath" states as may occur when there is a strong coupling between two electronic surfaces. We want to consider the case where the heat-bath states are part of a regular quantum spectrum, so the diagonal matrix elements are chosen to have Poisson spacing statistics. Coupling matrix elements to the bright state are chosen from a Gaussian distribution with zero mean. This work is complementary to an earlier study by Brody *et al.*,¹⁰ where the bath-state energies were chosen as the eigenvalues of GOE matrices.

This study determines the degree to which strong and random coupling to one basis state can turn a regular eigenvalue spectrum (Poisson statistics) into an irregular spectrum (GOE statistics). Tests for eigenstate repulsion and spectral rigidity indicate that level repulsion occurs only at very small spacings, and that the Δ_3 values are intermediate between Poisson and GOE values. The distribution of eigenvalues remains much closer to the initial Poisson distribution than to a GOE distribution. This result has important implications for a number of experiments that probe the level structure of high vibrational states of molecules through their mixing with a single bright vibronic state.^{11,12}

MODEL

Consider a diagonal matrix with ordered eigenvalues E_i ($i = 1, N$) (bath states). Add one row and column (the

bright state), with diagonal matrix element E_0 , and real off-diagonal coupling matrix elements H_{i0} . The eigenvalues of the matrix are solutions to the following equation:

$$F(\lambda) = E_0 - \lambda - \sum_i H_{i0}^2 / (E_i - \lambda) = 0. \quad (1)$$

The eigenvectors, for a given solution λ_k , are given by

$$a_i^k = -a_0^k H_{i0} / (E_i - \lambda_k), \quad (2)$$

$$(a_0^k)^{-2} = 1 + \sum_i H_{i0}^2 / (E_i - \lambda_k)^2. \quad (3)$$

The absorption spectrum due to the bright state is then

$$A(E) = \sum_k \mathcal{A}_k \delta(E - \lambda_k), \quad (4)$$

where $\mathcal{A}_k = (a_0^k)^2$, or for the Fourier transform test discussed later, $\mathcal{A}_k = 1$. $F(\lambda)$ has exactly one root in each of the open intervals $(-\infty, E_1)$, (E_i, E_{i+1}) , $(E_N, +\infty)$. Movement of eigenvalues are thus bounded by the positions on the unperturbed eigenvalues.

In our study, the bath states E_i were given Poisson spacing statistics with unit average spacing by taking $E_{i+1} = E_i - \ln(r)$, where r is a random number distributed uniformly between 0 and 1. The origin of energy was $E_1 = 0$, and the bright state energy E_0 was set equal to $E_N/2$. The coupling matrix elements were $H_{0i} = Hs_i$, where s_i are Gaussian random numbers with zero mean and unit standard deviation. In our simulation we took $N = 600$, $H^2 = 600$. Roots of Eq. (1) were determined to better than 10^{-8} energy unit accuracy. Only the central 301 eigenvalues out of 600 were chosen to minimize effects of matrix truncation. For the central eigenvalues and eigenvectors, contributions from states far above and far below a given state approximately cancel.

RESULTS

Figure 1 shows the eigenvalue spacing distribution obtained from 300 000 eigenvalue spacings (one thousand matrices) counted with a bin resolution of 0.005 average spacing units. Also shown in Fig. 1 are a Poisson and a Wigner distribution. The observed distribution displays level repulsion, but clearly looks more like a Poisson than a Wigner distribution over most of its range. We fit the observed distribution to a two-parameter form suggested by Brody,¹³ $P(s) = As^w \exp(-\alpha s^u)$, using uncertainties proportional to $\sqrt{P(s)}$, as calculated from counting statistics. The best fit values are $w = 0.629(10)$ (1σ) and $u = 0.860(7)$. The values of A (3.2286) and α (1.9669) are then determined by the requirement that $P(s)$ be normalized and have unit average. The fit of this function to the distribution cannot be distinguished from exact on a statistical basis. The standard deviation of the residuals of the fit differs from its calculated value by less than half its calculated uncertainty. A fit of all calculated spacings less than 0.045, without using bins, gives an almost identical threshold law of $P(s) \sim s^{0.625}$. The one-parameter Brody distribution fixes $u = w + 1$. This form yields $w = 0.2976$, but gives a poor fit. The distribution function recently determined by Berry and Robnik¹⁴ gives a poorer

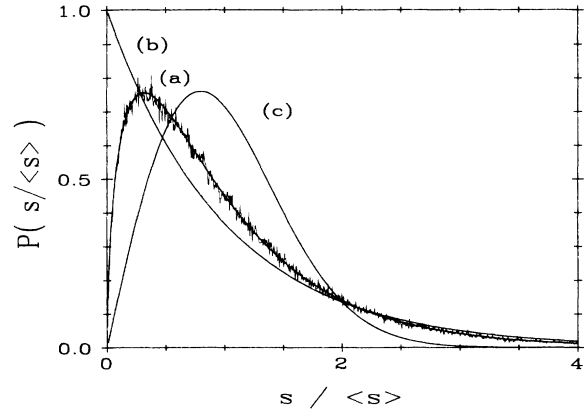


FIG. 1. Level-spacing distribution functions: (a) the model Hamiltonian (with two-parameter fit), (b) for a Poisson process, and (c) for the Gaussian orthogonal ensemble (GOE)—Wigner's approximation. The spacing axis is in units of mean level spacing. Model results are based on 300 000 spacings. The function form used in the model fit is discussed in the text.

fit than the Brody distribution. A smaller calculation with $\langle H^2 \rangle = 150$ gives a distribution that by eye overlaps the present one to within the noise. We conclude that the distribution function is stable to further increases in the coupling strength.

The level spacing distribution function expected under the constraints of the bounding of the eigenvalues but showing the greatest level repulsion occurs if each eigenvalue moves to the middle of the bounding interval. Such an eigenvalue spectrum has a spacing distribution function of $P(s) = 4se^{-2s}$. Such a distribution is much less like a Poisson distribution function than the observed one. In particular, that function displays linear eigenvalue repulsion near the origin, like the Wigner distribution function. Both the nonlinear threshold behavior of the observed distribution function and the accurate fit to a simple two-parameter form were unexpected and are yet unexplained.

As a test of the spectral "rigidity" of the eigenvalues, we computed Dyson and Mehta's $\Delta_3(L)$.¹⁵ We averaged $\Delta_3(L)$ over the energy spectrum according to the method of Bohigas *et al.*¹⁶ For Poisson statistics, $\Delta_3(L)$ averages to $L/15$, while for the GOE, $\Delta_3(L)$ averages to $[\ln(L) - 0.0687] / \pi^2(13)$. Table I shows $\Delta_3(L)$ calculated for $L = 5, 10, 15, 20$, and 25 . The uncertainty in the model $\Delta_3(L)$ values, due to finite sampling, is less than 0.01. We see that while the spectrum has some rigidity

TABLE I. Comparison of average $\Delta_3(L)$ values for simulation, Poisson, and GOE distributions.

L	Poisson	Simulation	GOE
5	0.333	0.222	0.156
10	0.667	0.527	0.226
15	1.000	0.808	0.267
20	1.333	1.098	0.296
25	1.667	1.395	0.319

[decreased $\Delta_3(L)$], the $\Delta_3(L)$ values are closer to those from a Poisson distribution than those from the GOE. This result can be rationalized by the bounding of eigenvalues between those of the initial Poisson distribution. This limits the amount of long-range order that the spectrum can achieve. In fact, the rigidity displayed by the spectrum at $L \sim 20$ is a surprising result.

Recently, Leviandier *et al.*¹⁷ have introduced another test for the spectral rigidity which is applicable even in the case of superimposed, independent distributions. They look at the Fourier transform (FT) of the eigenspectrum, $F[A(E)](t)$. The power spectrum of the spectrum, $|F[A(E)](t)|^2$ is the sum of two terms, one which decays on the time scale t_f equal to the inverse of the full width of the sampled spectrum, and another which is proportional to $[1 - b_2(t)]$, where $b_2(t)$ is the FT of the two-level cluster function $Y_2(s)$ [a prefactor is 1 if we take $\mathcal{A}_k = 1$ in Eq. (4)]. $Y_2(s) = 0$ for an eigenspectrum with Poisson statistics, so the power spectrum is constant, but modulated by speckle (interference between uncorrelated lines). For eigenstates from the GOE, $1 - b_2(t)$ is zero for $t = 0$ and rises to approximately 1 for t greater than the density of states ρ . Thus the power spectrum displays a ‘‘correlation hole,’’ falling to near zero following the initial decay and then rises to the Poisson result for $t_f < t < \rho$. For times longer than ρ there is no difference in the power spectra of Poisson and GOE distributions. We have averaged the power spectra obtained from the eigenvalues of the 1000 matrices. This average power spectrum, computed at points spaced by 0.01, where the time unit is the density of states, is shown in Fig. 2. The power spectrum is again like that for a Poisson distribution, except for a gradual dip at intermediate times, weaker than the deep dip seen with the GOE distribution. This dip extends to longer times than the density of states. This is consistent with the observed level spacing distribution which only deviates from a Poisson distribution for short times, so the effect on the power spectrum is at longer times. Since the Fourier-transform method can be applied to cases where individual lines cannot be observed,¹⁵ this result shows that a weak dip in the power spectrum cannot be interpreted as long-range order unless

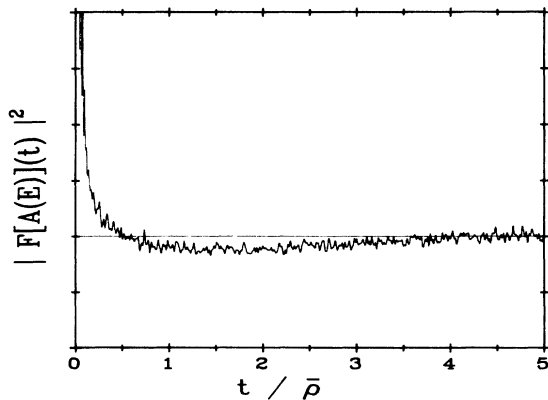


FIG. 2. The power spectrum of the simulated eigenspectra averaged over the 1000 sets of 301 eigenvalues. The unit of time is the density of states. See text for discussion.

it extends to times short compared to the density of states.

As this Hamiltonian is meant to model a system where we can excite the bright state in some way, we have calculated the transition amplitudes a_0^k for the 301 000 eigenstates. The observed amplitude distribution is shown in Fig. 3. The distribution is strongly peaked at small amplitudes. It can be fitted very well with a distribution function of the form used above, but with $w = -0.3367(42)$ and $u = 1.36(14)$. The residuals of the fit exceed those expected from counting statistics. This fitted function can be contrasted with the Gaussian transition moment distribution predicted for the GOE and for irregular quantum states.¹⁸ The distribution is shown in units of the mean transition amplitude. We know of no model to predict what distribution function to expect. From the above distribution we calculate the function $F_{aa} = \langle a^2 \rangle^2 / \langle a^4 \rangle$ of Heller,¹⁹ which gives the fraction of phase space sampled by the time evolution of state E_0 if the nonstationary bright state is prepared and then allowed to evolve. For the large coupling strength used here, the average transition strength is uniform across the spectrum, so corrections for the spectral envelope, as discussed by Heller, are unnecessary. For the calculated transition-amplitude distribution, we found $F_{aa} = 0.23$. This value is not much different from the value of 0.33 expected for a Gaussian distribution, and close to the values near 0.20 recently observed in the optical spectrum of NO_2 .¹⁰ The Gaussian amplitude distribution has been suggested for the quantum mechanically irregular case, which would be expected to show level repulsion. Heller has warned that meaningful results for F_{aa} can only be obtained if one chooses as the initial state, a state that is ‘‘localized.’’ The strong, random coupling of the bright state to all the others could be interpreted to mean that it is ‘‘delocalized.’’ If real relaxation problems like the NO_2 case can have this type of coupling, then it may be misleading to apply Heller’s methods to the intensity distributions observed in those cases. If we look at the amplitudes of one of the bath basis states, we see from Eq. (2) that they are related to the amplitude of the bright

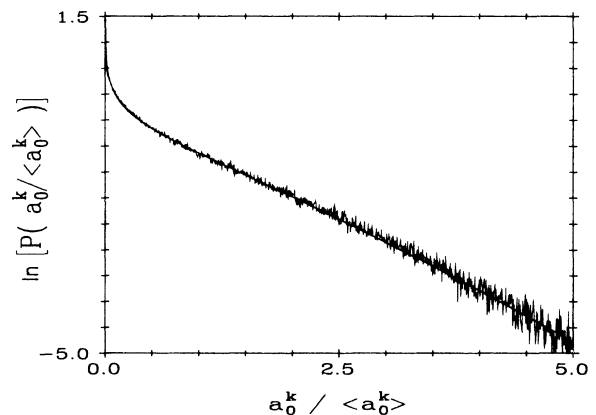


FIG. 3. The distribution function for the bright-state transition amplitudes, a_0^k , based on 1000 sets of 301 eigenstates. The transition amplitude is in units of the mean transition amplitude. The fitted functional form is discussed in the text.

state, but are multiplied by a "line shape" factor $H_{0i}/(E_i - \lambda_k)$. This strong localization of the amplitudes of a bath state to a few eigenstates near E_i means that Heller's F function cannot reasonably be applied to the bath states.

In recent articles Levine and co-workers²⁰ have examined an entropy measure of the transition-amplitude distribution function, and compared it to the entropy calculated for an intensity distribution given by a χ^2 distribution with a variable number of degrees of freedom ν . The ideal chaotic spectrum should have $\nu=1$, higher values of ν correspond to a decreased entropy and thus decreased chaos. From our fitted function for the transition-amplitude distribution, we calculate that entropy is the same as an intensity distribution function of $\nu=0.577$ or $\nu=2.08$. Only the smaller value of ν corresponds to a distribution diverging at the origin like ours.

CONCLUSIONS

The numerical results reported here demonstrate the small degree to which random couplings to one state can change the statistical properties of a regular quantum spectrum (Poisson statistics). The nature of the Hamiltonian significantly restricts the amount of long-range order the spectrum can develop, but the bounding of eigenvalues would allow significantly stronger eigenvalue repulsion. The transition amplitude distribution is strongly peaked at small intensities, but is, by Heller's F_{aa} test, largely "ergodic."

One of the most convenient experimental ways of studying the highly excited eigenstates of a quantum sys-

tem is by obtaining a high-resolution spectrum in the region of a "resonance," where the transition strength from some allowed transition is spread over a range of dark eigenstates which may be on a different electronic surface. Our present results demonstrate that if significant level repulsion or spectral rigidity is observed in these experiments, one can be confident that they are present in the heat-bath states considered without coupling to the state with transition strength. However, an ergodic spreading of the transition intensity over all the eigenstates may only represent "ergodicity" in the coupling, and may not indicate anything about the underlying dynamics that govern the heat-bath states. Such an ergodicity in the coupling may occur between "regular" quantum states if they are quantized about very different zero-order Hamiltonians or if the coupling are sufficiently complicated. Recent experimental work by the authors on the optical spectrum of NO_2 has demonstrated intensity ergodicity without any detectable level repulsion.²¹ It awaits further analysis to determine if a Hamiltonian of the type discussed here models this molecular system.

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