Molecular-Dynamics Approach to the Statistical Properties of Energy Levels

Xiazhou Yang and Joachim Burgdörfer
Department of Physics, University of Tennessee, Knoxville, Tennessee 37996-1200
and Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6377
(Received 20 August 1990)

The deformation of the energy-level spectra of quantum systems as a function of a control parameter governing the strength of a nonintegrable perturbation can be determined by standard molecular-dynamics techniques. The integration of Newton's equations of motion provides detailed information on the spectral deformation when the classical system undergoes a transition from mostly regular to mostly chaotic motion. This method is used to study the changes in the energy-level statistics and allows the direct determination of the Brody parameter in the predominantly chaotic regime.

PACS numbers: 05.45.+b, 31.15.+q, 33.10.Gx, 34.10.+x

Investigations of fingerprints of classical chaos on the quantum mechanics of seemingly simple nonintegrable Hamiltonian systems[1] continue to attract an increasing amount of interest. An impressive array of results on the distribution of energy levels,[2] on the nodal pattern of wave functions,[3] on the relation between unstable periodic orbits and scars of wave functions and level clustering,[4] and on the quantum suppression of diffusion in periodically perturbed time-dependent quantum systems[5] has become available.

Statistical properties of energy levels, in particular the nearest-neighbor-spacing (NNS) statistics, have proven to be very sensitive to the dynamical properties of the underlying classical system.[6] Berry and Tabor[7] proved rigorously that, except for special cases (one-dimensional systems and harmonic oscillators), the NNS distribution for a classically regular system is Poissonian. For classically chaotic systems there is strong numerical evidence that the NNS distribution for a real Hamiltonian system follows the prediction by the random-matrix theory for the Gaussian orthogonal ensemble[8] (GOE), though a rigorous proof is still missing.

Consider a generic two-degree-of-freedom nonintegrable Hamiltonian of the form

$$H=H_0+\lambda V, \tag{1}$$

where H_0 is a separable Hamiltonian and V is, in general, a nonseparable perturbation. For the vanishing control parameter $\lambda=0$, the classical motion is regular and the NNS statistics of the quantized system is Poissonian. As the control parameter is increased, the classical dynamics undergoes a transition from mostly regular to mostly chaotic motion. It has been found empirically that the NNS statistics in the transition regime is reasonably well described by a Brody distribution[8]

$$P(S)=AS^q\exp(-BS^{1+q}), \tag{2}$$

where S is the NNS in units of the mean level spacing, $A=(1+q)B$, $B=\Gamma^{1+q}((2+q)/(1+q))$, and q is found by fitting the "experimental" NNS distribution with a distribution of the form (2). The Brody distribution interpolates between the Poissonian distribution ($q=0$) and the Wigner (approximate GOE) distribution ($q=1$). As λ increases, q should (not always monotonically) increase from 0 to 1. A microscopic analysis of the behavior of the Brody parameter $q(\lambda)$ appears to be missing.

Intriguing qualitative explanations for the chaotic limit ($q=1$) were given by Pechukas,[9] Yukawa,[10] and Berry[11] treating the set of energy levels as an interacting many-body system and invoking the notion of equilibrium statistical mechanics. The latter approach goes back to Dyson's observation[12] that different ensembles of random-matrix theory can be mapped onto the equilibrium statistical mechanics of a one-dimensional Coulomb gas on a circle at different temperatures embedded in a two-dimensional space.

In this Letter we report on the first study of the evolution of the level statistics in the transition region between the regular and chaotic limits based on the solution of the well-known set of coupled ordinary differential equations[9,10]

$$\frac{d}{d\lambda}x_n=\langle n|V|n\rangle=V_{nn}=p_n, \tag{3a}$$

$$\frac{d}{d\lambda}p_n=2\sum_{i\neq n}\frac{V_{in}^2}{x_n-x_i}, \tag{3b}$$

$$\frac{d}{d\lambda}V_{in}=\sum_{j\neq i,n}V_{ij}V_{jn}\left(\frac{1}{x_i-x_j}+\frac{1}{x_n-x_j}\right)-\frac{V_{in}(p_i-p_n)}{x_i-x_n}, \tag{3c}$$

where $x_n(\lambda)=\epsilon_n(\lambda)$ are the energy levels, and we have assumed the coupling matrix V_{in} to be real and the spectrum to be entirely discrete. Extensions to Hermitian matrices and to the continuum[13] are straightforward. Equations (3) follow from (1) by forming expectation values and differentiation with respect to λ. This set is an obvious generalization of the Hellman-Feynman theorem [Eq. (3a)] and will be referred to in the following as Hellman-Feynman equations (HFE) of motion. They describe the evolution of the energy levels under

variation of the control parameter λ completely. We have developed a code to numerically integrate Eqs. (3) for a large number of energy levels (presently up to 10^4 levels).[14] Our approach is directly modeled after molecular-dynamics (MD) calculations for classical liquids.[15] We identify λ as "time" and (3) as Newton's equations of motions for N particles with canonical coordinates (x_n,p_n), each particle representing one energy level. The initial conditions $[x_n(0),p_n(0),V_{in}(0)]$ are provided by H_0. The only nonstandard feature in (3) is the additional degrees of freedom of fluctuating "charges" $V_{in}(\lambda)$ described by Eq. (3c). We chose a chainlike configuration where the position coordinates, the energy levels, form an ordered sequence $(x_1 < x_2 \cdots < x_n)$ which will be conserved because of the singular repulsive forces between levels of given exact symmetry. At the lower end of the chain (x_1) we always use open boundary conditions while at the upper end (x_N), suitably prescribed boundary conditions[13] can reduce errors which result from the truncation of the levels $n > N$. Matrix diagonalization would correspond to open boundary conditions also at the top of the chain.

In a standard MD calculation the propagation of ensembles is facilitated by the fact that the number of $N(N-1)/2$ mutual interactions in the N-particle system can be reduced to those within a reaction range of J nearest neighbors provided the forces are sufficiently short ranged. The number of interacting pairs of particles is thus reduced from $N(N-1)/2$ to $N\times J/2$, where $J \ll N$. Application of such a reaction window to the HFE implies the use of a λ-dependent self-adjusting "banded" Hamiltonian matrix, which is crucial in gaining computational speed. However, the forces in (3) are short ranged only if $V_{in}(\lambda) \to 0$ as $|i-n| \gg 1$. We therefore find the convergence as a function of the reaction range to be rather slow for individual levels (typically, $J \approx 50$); however, it is much faster for ensemble properties. The present method monitors the deformation of the quantal spectrum continuously and is well suited for identifying changes of the level distribution as a function of the control parameter. We emphasize that the present approach is fully quantum mechanical despite its classical appearance.

As a model system for the eigenvalue dynamics we use the Hamiltonian for two coupled Morse oscillators with[16]

$$H_0 = \sum_{i=1}^{2} H_0^i , \quad H_0^i = P_i^2/2M_i + V_i(r_i) , \tag{4a}$$

and

$$V = -P_1P_2/m . \tag{4b}$$

This system provides a simple model for the vibronic motion of linear triatomic molecules and has been extensively studied as a model for the quantum mechanics of a classically chaotic system with two degrees of freedom.[17] In (4), M_i are the reduced masses for the two diatomic pairs in the molecule, V_i are the corresponding Morse potentials, and m is the mass of the central atom. We use the molecular parameters for H-C-C. However, in order to improve the statistics we have arbitrarily rescaled $\hbar$ to $\hbar/3$ thereby increasing the number of bound states below the dissociation limit to 1485. The coupling to the continuum is neglected.

Recently, Nakamura and Lakshmanan[18] have shown that Eq. (3) constitutes an integrable Moser-Calogero system with an internal complex vector space possessing a complete set of constants of motion. Notions of equilibrium statistical mechanics for the level distribution implicitly invoking ergodicity (or even mixing) appear, at first glance, hardly justified. Yukawa[10] suggested that ergodicity is restored due to the introduction of boundary conditions imposed on (3) which reduce the number of constants of motion. However, since boundary conditions are characteristics of the model-dependent truncation of the Hilbert space rather than of the Hamiltonian itself, it is unsatisfactory to rely on model-dependent approximations in order to approach an "equilibrium" level distribution which is considered to be generic for nonintegrable systems. We therefore use in the following the MD method to test the equilibrium-statistical-mechanics hypothesis.

We note first that the canonical equations of motion for the $2N$ phase-space coordinates (x_n,p_n) are generated from an effective λ "time"-dependent model Hamiltonian,[11]

$$\tilde{H}(\lambda) = \sum_{n=1}^{N} \frac{p_n^2}{2} - 2\sum_{i<n}^{N} V_{in}^2(\lambda) \ln|x_i - x_n| . \tag{5}$$

Equation (5) represents a Hamiltonian for a one-dimensional Coulomb gas coupled to a heat bath with $N(N-1)/2$ degrees of freedom through λ-dependent coupling parameters ("charges") $V_{in}(\lambda)$. In the semiclassical limit, $N \to \infty$, the reduced density function of a small system (with $2N$ degrees of freedom) coupled to a reservoir with $\sim N^2/2$ degrees of freedom is expected to be canonical,

$$P(\tilde{H}) = \exp[-\beta\tilde{H}] = \exp\left[-\frac{\beta}{2}\sum_{i=1}^{N} p_i^2\right] \times \exp\left[2\beta \sum_{i<n} \langle V_{in}^2\rangle \ln|x_i - x_n|\right] . \tag{6}$$

The essential assumption underlying (6) is that the coupling to the reservoir through rapidly fluctuating "charges" $V_{in}(\lambda)$ is sufficiently strong that equilibrium is attained within the available physical λ time (i.e., strength of the nonseparable perturbation). Furthermore, replacement of V_{in}^2 by its average $\langle V_{in}^2\rangle$ requires that the fluctuations are fast on the time scale of the motion in the $2N$ phase space. The origin of these rapid fluctuations is close collisions (i.e., avoided crossings) between adjacent energy levels.

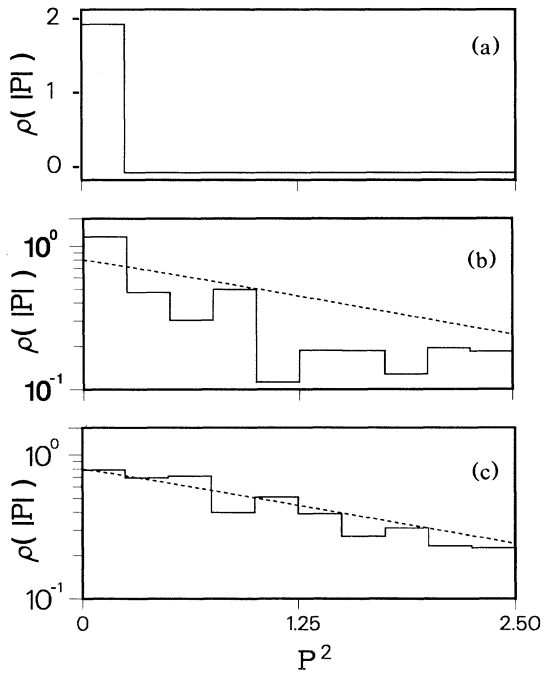

FIG. 1. Histogram of the single-particle kinetic-energy distribution at three different "times" (a) $\lambda=0$, (b) $\lambda=0.10$, and (c) $\lambda=0.65$. (---) Boltzmann distribution with temperature $\beta^{-1}=\langle p^2-\langle p\rangle^2\rangle$.

Tracing out all positive coordinates, Eq. (6) predicts a Maxwell-Boltzmann distribution for the single-particle kinetic energy. A test for a Maxwell-Boltzmann distribution has the advantage that it does not explicitly involve the properties of the fluctuating charges $V_{in}^2(\lambda)$. Figure 1 displays the distribution of the kinetic energies at various λ times. Note that the peak at zero momentum (all $p_n=0$) at $\lambda=0$ is a peculiarity of the system of coupled Morse oscillators. With increasing λ the distribution indeed approaches a Maxwell-Boltzmann distribution represented in Fig. 1 by a straight line with temperature

$$\beta^{-1}=\langle p^2-\langle p\rangle^2\rangle . \tag{7}$$

Figure 2(a) displays the temperature, the ensemble averages $\langle V_{in}^2\rangle$, and the subset of nearest-neighbor couplings $\langle V_{n,n+1}^2\rangle$ as a function of λ, while Fig. 2(b) gives χ^2 for a fit with a Maxwell-Boltzmann distribution. Obviously, equilibrium is reached for $\lambda\approx 0.6$ as reflected in both an approximately constant value of β^{-1} and small χ^2 values. The ensemble averages $\langle V_{in}^2\rangle$ show remarkably little variation as a function of λ.

The joint particle- (level-) distribution function follows from (6) upon tracing out all momentum coordinates,

$$P(x_1,\ldots,x_n)=\prod_{i<n}|x_i-x_n|^{2\beta\langle V_{in}^2\rangle} . \tag{8}$$

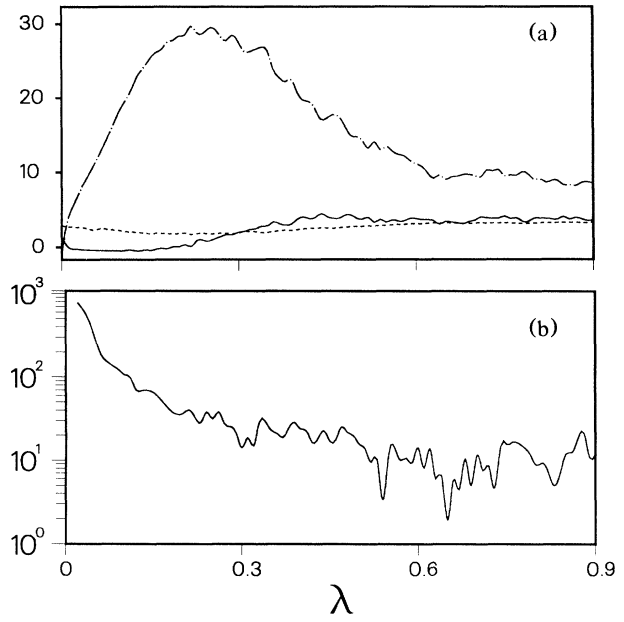

FIG. 2. (a) Temperature β^{-1} (-·-·), $\langle V_{in}^2\rangle$ (---), and $\langle V_{n,n+1}^2\rangle$ (——). (b) χ^2 for a Maxwell-Boltzmann distribution as a function of λ.

Equation (8) agrees with the GOE prediction if the exponent in (8) happens to attain the value

$$2\beta\langle V_{in}^2\rangle=1 . \tag{9}$$

For arbitrary exponents Eq. (8) implies for the NNS distribution [Eq. (2)] locally

$$P(S)\underset{S\to 0}{\propto} S^{\gamma_1} \tag{10}$$

with

$$\gamma_1=2\beta\langle V_{n,n+1}^2\rangle . \tag{11}$$

Extending (10) to large S using the standard procedure for deriving the Wigner distribution[19] yields a Brody-like distribution [Eq. (2)] with γ_1 playing the role of the Brody parameter q. The important result is that γ_1 can be directly determined in terms of the equilibrium kinetic and potential energies of the Coulomb-gas Hamiltonian [Eq. (11)] provided that equilibrium has indeed been reached. In turn, if $\gamma_1\approx q$, a direct numerical determination of the Brody parameter becomes possible.

Figure 3 displays both the Brody parameter q determined from fits with NNS distributions and γ_1 determined from Eq. (11) together with the fraction q_{cl} of the relatively narrow classically chaotic phase space. For the classical calculation we used initial conditions on the energy hypersurface which lies approximately in the center of the stretch from the 400th to the 1000th quantal eigenvalue entering the statistics ($E\simeq 0.75\pm 0.1$ in units of the dissociation energy). We note first that the transi-

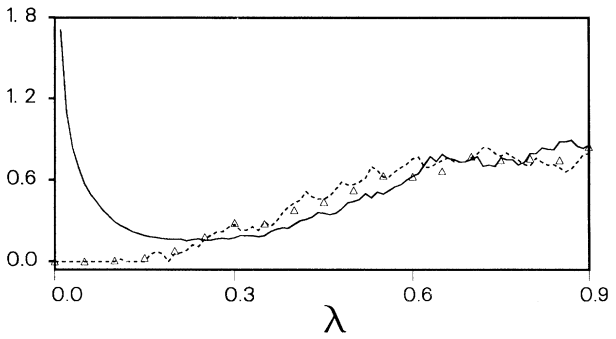

FIG. 3. Brody parameter q (---), γ_1 (——), and fraction of classically chaotic phase space q_{cl} (△) as a function of λ.

tion to classical large-scale chaos ($q_{cl} \gtrsim 0.6$) occurs simultaneously with the approach of statistical equilibrium of the energy-level distribution as described by the HFE ($\lambda \gtrsim 0.6$). At the same time the exponent γ_1 agrees well with the Brody parameter q determined from fits to histograms, in agreement with the hypothesis (11). In line with other investigations[17] we find that q (or γ_1) stays below the GOE predictions, probably because of residual islands of regular motion. In the near regular regime ($\lambda < 0.5$) the ensemble is far from statistical equilibrium and γ_1 deviates strongly from q. Contrary to previous assumptions,[10] the Poissonian distribution cannot be derived from equilibrium statistical mechanics for the HFE. The latter is a consequence of the fact that in the regular regime avoided crossings become crossings. In this limit the N-body system behaves like a collision-free gas which does not attain equilibrium.

In summary, the first detailed numerical of the Hellman-Feynman equation for the motions of energy levels confirms that the nearest-neighbor-spacing distribution approaches a statistical-equilibrium distribution for large values of the control parameter for the non-separable perturbation. The nearest-neighbor-spacing distribution approaches a Brody-type distribution with a Brody exponent q close to but not coincident with the value for the Wigner (or GOE) distribution. The Brody parameter can be determined directly from equilibrium properties of the N-body Hamiltonian which generates the HFE [Eq. (11)]. We expect the same to be true for the exponent q of level repulsion in other interpolation formulas for the nearest-neighbor spacings which have a power-law limit $P(S) \propto S^q$ for $S \to 0$. In the regular regime, on the other hand, the level distributions can only be determined from the nonequilibrium solution of the HFE.

We have observed that in the chaotic regime large fluctuations persist and subensemble averages $\langle V_{in}^2 \rangle$ for different $|i-n|$ show systematic deviations. Both observations indicate deviations from a GOE joint-probability-distribution function [Eq. (8)] and the persistence of long-range correlations in the spectra.

This work was supported in part by the National Science Foundation and by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract No. BE-AC05-840R21400 with Martin Marietta Energy Systems, Inc.

[1]M. V. Berry, Phys. Scr. **40**, 335 (1989).

[2]S. McDonald and A. Kaufman, Phys. Rev. Lett. **42**, 1189 (1979); O. Bohigas, M. Giannoni, and C. Schmit, Phys. Rev. Lett. **52**, 1 (1984); E. Haller, H. Köppel, and L. Cederbaum, Phys. Rev. Lett. **52**, 1665 (1984); T. Seligman, J. Verbaarschot, and M. Zirnbauer, Phys. Rev. Lett. **53**, 215 (1984).

[3]M. Shapiro and G. Goelman, Phys. Rev. Lett. **53**, 1714 (1984).

[4]M. Gutzwiller, J. Math. Phys. **12**, 343 (1971); E. Heller, Phys. Rev. Lett. **53**, 1515 (1984); V. Bogomolny, Physica (Amsterdam) **31D**, 169 (1988).

[5]T. Hogg and B. Huberman, Phys. Rev. A **28**, 12 (1983).

[6]B. Eckhardt, Phys. Rep. **163**, 205 (1988).

[7]M. V. Berry and M. Tabor, Proc. Roy. Soc. London A **356**, 375 (1977).

[8]T. A. Brody, J. Flores, J. B. French, P. A. Mello, A. Pandey, and S. S. M. Wong, Rev. Mod. Phys. **53**, 385 (1981).

[9]P. Pechukas, Phys. Rev. Lett. **51**, 943 (1983).

[10]T. Yukawa, Phys. Rev. Lett. **54**, 1883 (1985).

[11]M. V. Berry, in *Chaotic Behavior in Quantum Systems,* edited by G. Casati (Plenum, New York, 1985), p. 123.

[12]F. Dyson, J. Math. Phys. **3**, 140 (1962).

[13]X. Yang and J. Burgdörfer (to be published).

[14]We note that a sample calculation involving 10–100 levels was recently discussed by W. Steele, S. Brits, and A. van Tonder, J. Phys. A **21**, 2657 (1988).

[15]A. Rahman, Phys. Rev. **136**, A405 (1964); L. Verlet, Phys. Rev. **159**, 98 (1967).

[16]W. Smyser and D. Wilson, J. Chem. Phys. **50**, 182 (1969).

[17]V. Buch, R. Gerber, and M. Ratner, J. Chem. Phys. **76**, 5397 (1982); T. Terasaka and T. Matsushita, Phys. Rev. A **32**, 538 (1985).

[18]K. Nakamura and M. Lakshmanan, Phys. Rev. Lett. **57**, 1661 (1986).

[19]See, e.g., M. Mehta, *Random Matrices* (Academic, New York, 1967).