REPRINTED FROM:

CHEMICAL PHYSICS LETTERS

Volume 73, No. 2, 15 July 1980

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pp. 269–272

NORTH-HOLLAND PUBLISHING COMPANY – AMSTERDAM

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Received 26 March 1980; in final form 22 April 1980

In plots of eigenvalues of the Schrödinger equation versus a perturbation parameter, many avoided crossings are found in the classically stochastic regime for the system studied. None were observed in the classically quasi-periodic regime. Overlapping avoided crossings are suggested as a mechanism for making the vibrational wavefunction a "statistical" one.

In recent years there have been numerous investigations, both numerical and analytical, of classical hamiltonian systems [1]. Typically, they behave quasi-periodically at low energies and stochastically ("chaotically") but deterministically at high energies [1]. We have pointed out that in the corresponding quantum-mechanical systems, plots of energy eigenvalues versus a perturbation parameter should be very useful in providing an analysis independent of basis set and of choice of coordinates. We suggested that a regime of many overlapping avoided crossings (anti-crossings) would provide a mechanism for "quantum-mechanical stochasticity" [2,3]. As discussed there, in this vein, *isolated* avoided crossings do not imply "stochasticity" [2,3].

In the present paper, we illustrate this behavior for a system of three coupled anharmonic oscillators with a hamiltonian

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + p_z^2 + \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) + K_{122}xy^2 + K_{133}xz^2 + K_{233}yz^2 + K_{111}x^3 + K_{222}y^3 + K_{1122}x^2y^2 + K_{2233}y^2z^2, \quad (1)$$

with parameters given in table 1. Thereby, we have a 1:1 zeroth order resonance and a 1:2 (Fermi) resonance. The hamiltonian was diagonalized using the program EISPAC ‡, with a harmonic oscillator basis set consisting of product functions

Table 1
Parameters for hamiltonian (1)

$\omega_x = 2$	$K_{111} = -0.01$
$\omega_y = 1$	$K_{222} = -0.01$
$\omega_z = 1$	$K_{122} = -0.10 - -0.16$
$K_{1122} = 0.05$	$K_{133} = -0.10$
$K_{2233} = 0.05$	$K_{233} = -0.10$

* Contribution No. 6188 from the California Institute of Technology.

‡ EISPAC is a package developed by National Activity to test software. See, for example, ref. [4].

$$\psi = \sum\sum\sum \psi_x \psi_y \psi_z , \qquad (2)$$

summed over the quantum numbers.

The hamiltonian (1) is even in z and eigenvalues were only calculated with a basis set with even functions of z; i.e., $n_z = 0, 2, 4, \ldots$. For this calculation ten n_x functions, fourteen n_y and n_z functions were used. Because ω_x is larger, a fewer number of x functions were needed than y and z ones. Calculations for which $\psi(x, y, z) = -\psi(x, y, -z)$ were not made.

In figs. 1–3, the eigenvalues E are plotted versus K_{122} for three ranges of energy. In the lower range, fig. 1, no avoided crossings are observed. Above a certain energy there are an increasing number of *overlapping* avoided crossings, as in figs. 2 and 3. These figures were drawn through points at $-K_{122} = 0.10, 0.11, \ldots, 0.16$, and hidden symmetries were assumed absent. In that case there are no curve crossings, since curve crossings would then correspond to a conical intersection in a energy versus multidimensional parameter space, and such crossings would be of "measure zero". As a test, an "avoided crossing" in the vicinity of an (E, K_{122}) value (15.1, −0.13) was examined using a fine grid of K_{122} values, and found to be an "avoided" crossing. The results are given in table 2. The crossing would have occurred at $K_{122} = -0.131$.

We estimated the energy region for the onset of classical stochasticity, using classical trajectory spectra as a guide [5]. The spectrum has numerous "banded

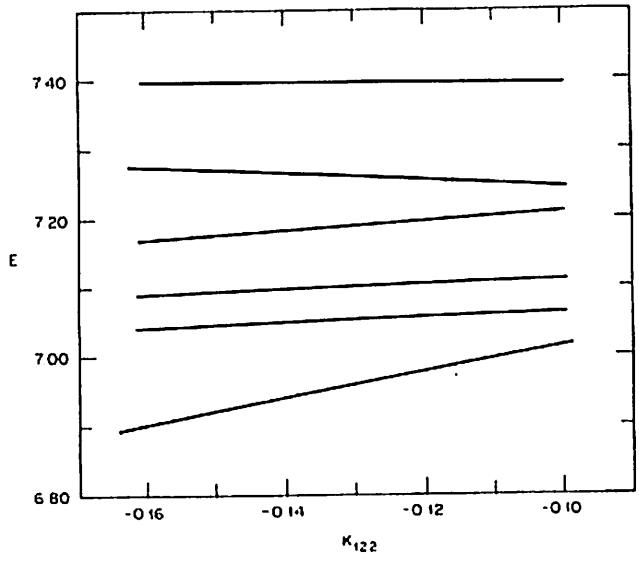

Fig. 1. A correlation diagram for E versus K_{122} in the quasi-periodic regime.

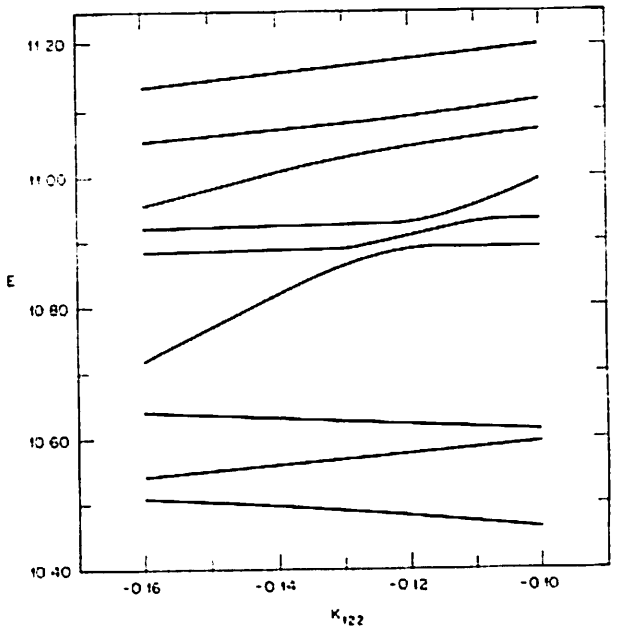

Fig. 2. As in fig. 1, but in an energy range near the classical quasi-periodic stochastic boundary.

regions" in the stochastic regime and relatively few lines in the quasi-periodic regime [2,5]. By this criterion for classical stochasticity, the trajectories for hamiltonian (1) were found to be stochastic commencing at an energy of about 11.0. At $E = 13$, many trajectories of a random sample produced stochastic type motion. In a random sample of 200 trajectories at $E = 20.0$, no escape was observed. Escape occurs at $E = 25$, and probably at a somewhat smaller E. Since $E_{esc} \approx 20$ and $E_{stochastic} \approx 12$, the system has a large

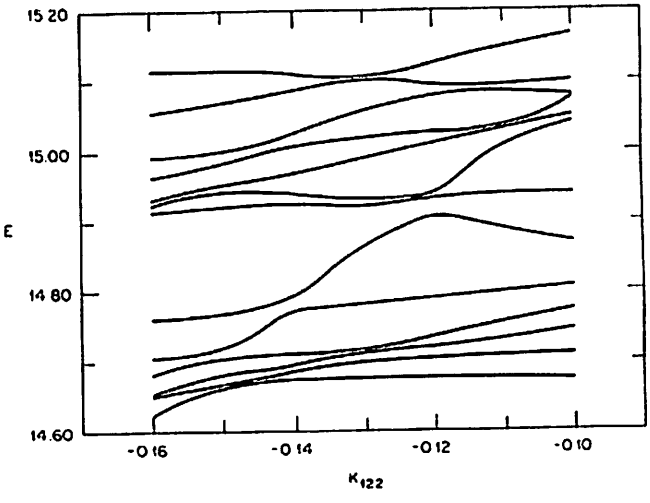

Fig. 3. As in fig. 1, but at a higher energy range.

Table 2
Energy of two states versus a parameter K near an avoided crossing

$-K_{122}$	E_{141}	E_{142}
0.120	15.094	15.126
0.128	15.100	15.108
0.130	15.100	15.105
0.132	15.099	15.104
0.140	15.086	15.109

classically stochastic regime, and many quantum states in it for study.

The behavior in figs. 2 and 3 contrasts markedly with that which we found [2] for the Hénon–Heiles system [6], namely eq. (1) with p_x and x absent, $K_{2233} = 0$, and with $K_{222} = -\frac{1}{3}K_{223}$. There, even in the classical "stochastic" regime [5] regular eigenvalue sequences and only one isolated avoided crossing were found for the parameter employed [2]. By such a spectral criterion for lack of stochasticity, one would judge that classical stochasticity does not in itself imply quantum stochasticity. It depends on the size of h. One would anticipate a correspondence when $h \to 0$. (Evidence in this point is given later in the paper.)

One difference between systems of three or more coordinates, with smoothly varying potentials, compared with two-coordinate ones, apart from the fact that they can represent molecules more realistically, lies in a difference in their classical transition behavior from the classical quasi-periodic to stochastic regime. In the two-coordinate case, "chaotic trajectories" are confined between residual invariant tori and so cannot explore all of phase space at the given energy.

We suggested [7] that in a quantum-mechanical stochastic region the average of any dynamical quantity $X(q,p)$ should begin to approximately equal the corresponding classical phase-space microcanonical average of X at that energy, provided X does not heavily weight the classically forbidden regions. At a sufficiently high density of states, one would also expect, as a criterion of quantum stochasticity, that the average of $X(q,p)$ over a quantum-mechanical state of energy E would approximate the microcanonical average over the states in a small interval $(E, E+\delta E)$ [3]. In the quasi-periodic case it will approximate instead the phase-space average on the torus which corresponds, semiclassically, to the given quantum state. Tests of this expectation are being undertaken using the wavefunctions obtained for the present system. We are also currently studying the relation between classical and quantum stochasticity for the hamiltonian (1).

Finally, we would like to comment on the relation of the present idea of avoided crossings to some other work in the literature related to quantum stochasticity, and also to provide preliminary evidence for the expectation that as $h \to 0$, overlapping avoided crossings correspond to classical chaos. We have seen [2] that avoided crossings produce large second differences in plots of eigenvalues versus perturbation parameter. Pomphrey [8] studied second differences for the Hénon–Heiles [6] potential using a value of h smaller than ours [2] and found many more cases of large second differences. In quantum-mechanical perturbation theory calculations we also observed [9] many more "zeroth-order crossings" (which yield avoided crossings upon use of degenerate perturbation theory near the crossing) for Pomphrey's h than for ours. Similarly, in classical perturbation theory calculations for the Barbanis potential [10] we have found [9], using a grid of action variables, an onset of "zeroth-order crossings" roughly at an energy where classical "chaos" begins.

Stratt et al. [11] in their investigation of the Barbanis potential [10] studied nodal patterns of quantum-mechanical wavefunctions and found for some states major changes of nodal patterns. We believe, and are currently testing this possibility, that these changes are each associated with avoided crossings. In this study it will be interesting to see whether the latter are isolated avoided crossings or overlapping ones. (Only the latter may prove to be associated with a "stochasticity".)

Nordholm and Rice [12] studied the wavefunctions ψ for the Hénon–Heiles [6] potential and examined their projections on those of the unperturbed (harmonic oscillator) basis set. When a ψ was substantially distributed over a number of the latter states it was termed "global", and was termed local otherwise. A state can appear to be global (a) not only when its wavefunction is "statistical" (sometimes labeled "stochastic", "ergodic", "chaotic") but also (b) when its shape is considerably distorted from the corresponding one of the unperturbed system. Indeed, we were able to find [13] classical invariant tori each of which corresponded individually semiclassically to many of the

"global" states, so that all of these particular global states certainly are of case (b). Even though globality is, therefore, not necessarily or even primarily due to stochastic behavior, it is very interesting in its own right. It provides information on the nature of the wavefunction relative to that of some unperturbed system. Because of the basis set dependence [12;13, section 6] of global versus local states, similar calculations were made [11] using natural orbitals as the basis set. The comparison is still a coordinate dependent one [14].

We plan to investigate in more detail the relation between the present concept of "avoided crossings", as a mechanism for quantum stochasticity, and these and the many other interesting related results ‡ on the behavior of eigenfunctions and eigenvalues.

The research was sponsored by the US Department of Energy under contract W-7405-eng-26 with the Union Carbide Corp. (at Oak Ridge), the National Science Foundation (at California Institute of Technology) and the DOE (at Sandia National Laboratories). We also wish to thank Dr. J. Sullivan and R. Lenius for their help in using the IBM 3033.

‡ One of us (RAM) is indebted to W.H. Miller for a discussion of this point.

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