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Stochastic Behavior in Classical and Quantum Hamiltonian Systems

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R. A. Marcus,[1], D. W. Noid[1] and M. L. Koszykowski[1]

Department of Chemistry
Noyes Laboratory
University of Illinois
Urbana, Illinois 61801

Abstract

Semiclassical studies on molecular bound states, molecular collisions, and time-dependent dynamical systems are described. Several methods have been evolved for determining the action variables of nonseparable bound state systems, and thereby for calculating their quantum mechanical eigenvalues. Nonresonant and resonant systems are included, and surfaces of section in higher (>2) dimensional as well as in two-dimensional systems are obtained. Further, from the Fourier transform of an autocorrelation function the molecular spectrum can be determined directly from a trajectory. The effect of an oscillating electric field on a molecule is discussed semiclassically with a view to obtaining a relation between the classical mechanical and quantum mechanical treatments.

1. Introductory Remarks

In the present paper we would like to describe some recent results obtained in the semiclassical theory of bound states of molecules, molecular collisions, and time-dependent phenomena. The theory permits one to use classical mechanical trajectories and quasi-periodic concepts to calculate quantum mechanical properties.

In the treatment of molecular collisions [1], the semiclassical wavefunction $\psi(q)$ of the coordinates q is expressed in terms of the phase integral S along a trajectory

$$\psi(q) \sim |\det \partial^2 S/\partial q \partial P| \exp(iS/\hbar) \tag{1.1}$$

$$S = \int_{q_0}^{q} p\cdot dq + p_0\cdot q_0 - (M\pi/2) \tag{1.2}$$

Here, p is the N-dimensional momentum conjugate to the N-dimensional coordinate q, with initial values of (p_0,q_0). $M\pi/2$ is the accumulated loss of phase due to the trajectory having been reflected from caustics or having passed through foci. The determinant in (1.1) is an N x N one. P denotes a set of constants of the motion--usually the action variables for the N-1 bounded degrees of freedom and the total energy E. (There is one unbounded coordinate, a radial distance coordinate, in molecular collisions.) $\hbar$ is Planck's constant divided by 2π.

When there is more than one topologically independent trajectory that proceeds to q, ψ consists of a sum of terms of the above form. The wavefunction over all space is obtained by appropriate choice of the q_0's. The action variables contained in P are the classical analogs of the quantum numbers n, and usually equal $(n+\frac{1}{2})h$, depen-

[1]Present addresses: California Institute of Technology, Pasadena, CA, Oak Ridge National Laboratory, Oak Ridge, TN, Sandia Livermore, Livermore, CA, respectively.

ding on the degree of freedom.

The semiclassical theory has been extensively reviewed for elastic collisions [2]--i.e., collisions which involve no interconversion of translational and internal motion. In most elastic collision studies it was possible to separate variables in the classical motion and so obtain p as a function of q. Since 1970 the major development [1] has been in the treatment of inelastic collisions [3]. Here, in these no longer separable systems the classical mechanical equations of motion are now integrated numerically using computers to obtain p(q). Once the wavefunction for the collision has thereby been determined one can calculate any desired properties associated with the collision, such as transition probabilities from one internal state of a molecule to another of its states. Some of these transitions are classical dynamically-forbidden but not energetically-forbidden, and then one uses trajectories in which p is a complex-valued function of q. One then obtains transition probabilities which are exponentially small.

We focus our attention in the present paper, however, on some results for bound state rather than collision problems, and finally we consider briefly a time-dependent problem such as occurs for a molecule in an intense coherent or incoherent light pulse.

2. Bound State Problems

In 1917 EINSTEIN [4] pointed out that to quantize a system one should find the topologically independent canonical invariants-- the $\oint p\cdot dq$ equal to $(n+\delta)h$, where δ is a known constant, typically 1/2 for nondegenerate vibrations. I.e.

$$\oint_{C_i} p\cdot dq = (n_i+\tfrac{1}{2})h \qquad (i = 1,\ldots,N), \tag{2.1}$$

where C_i are the topologically independent paths and N is the number of coordinates.

KELLER showed how to obtain in this way the quantum mechanical eigenvalues of the systems in which a particle moved in various shaped regions of constant potential energy inside and infinitely high at the boundary [5]. Until recently no method was available for determining these $\oint p\cdot dq$ integrals for nonseparable two or more dimensional systems when the potential energy function is smoothly varying. An example of a trajectory for such a system having a Henon-Heiles Hamiltonian (2.2) is given in Fig.1 for the case of incommensurate ω_x and ω_y.

$$H = \tfrac{1}{2}(p_x^2+p_y^2+\omega_x^2x^2+\omega_y^2y^2) + \lambda x(y^2+\eta x^2) \tag{2.2}$$

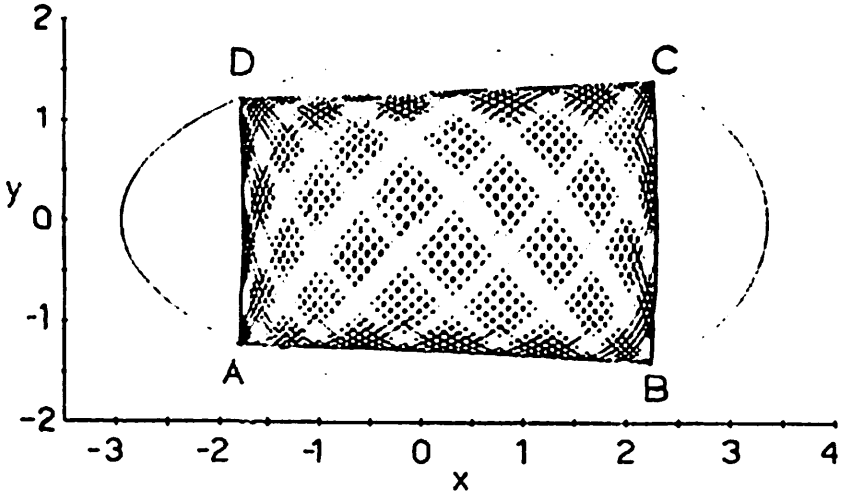

Fig.1 Trajectory for the Hamiltonian (2.2), with ω_x and ω_y incommensurate.

By integrating along the caustic in Fig.1 from A to B and back and also from A to C and back, EASTES in this laboratory was able to evaluate for the first time the two independent phase integrals [6]. Using an iteration procedure it was possible to find trajectories at energies such that (2.1) were simultaneously satisfied. Thereby, the quantum mechanical eigenvalues were determined.

The topologically independent paths C_i are also depicted for the Fig.1 system in Fig.2. NOID [7] made use of Poincaré surfaces of section to evaluate the phase integral. E.g., for the surface of section at y = 0 it is the area under the curve of p_x versus x. Results for the eigenvalues obtained in this way are given in Table I. Other methods [8] for obtaining the eigenvalues have been developed since. The methods tend to complement each other each other. (Table I is at end of paper.)

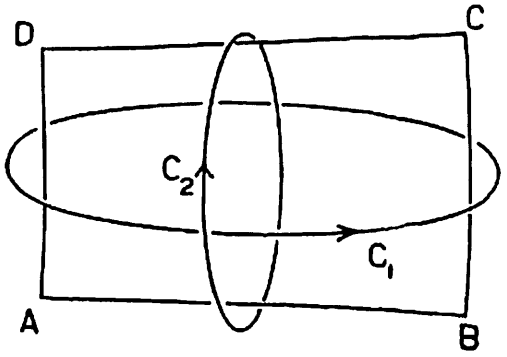

Fig.2 Topologically independent paths C_1 and C_2 for calculating action integrals for the trajectory in Fig.1

One sees from Fig.1 that when ω_x and ω_y are incommensurate the anharmonicity in (2.2) causes only a minor distortion of the original box-like shape and, correspondingly, only minor energy transfer between the degrees of freedom x and y. The situation is quite different when ω_x and ω_y are commensurate. When $\omega_x = \omega_y$ the trajectories are either of the librating or precessing type, an example of the latter being given in Fig.3. Curvilinear (e.g., radius=constant) and rectilinear (y = 0) surfaces of section were used to obtain the phase space data to evaluate the topologically independent phase integrals and again evaluate the quantum eigenvalues thereby [9].

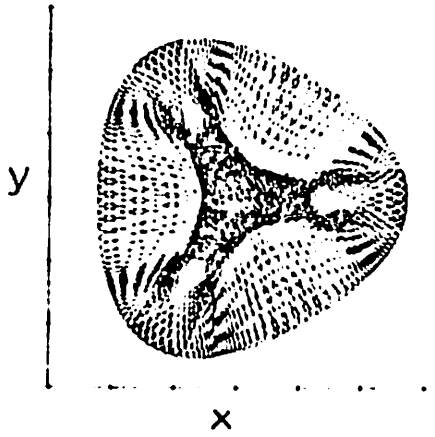

Fig.3 Trajectory for the Hamiltonian (2.2) with $\omega_x = \omega_y$

Another example showing extensive energy sharing between the x and y coordinates is the Fermi resonance case ($\omega_x = 2\omega_y$). Here a secular term in the anharmonic contribution can be shown to arise (unlike the $\omega_y = 2\omega_x$ case) and to cause the

extensive distortion, as in Fig.4, again unlike the $\omega_y = 2\omega_x$ case. Because of the shape of the region swept out in Fig.4 one surface of section was selected along a parabolic coordinate curve, and the other at y = 0, to evaluate the two independent phase integrals, and, thereby, to evaluate the quantum eigenvalues [10].

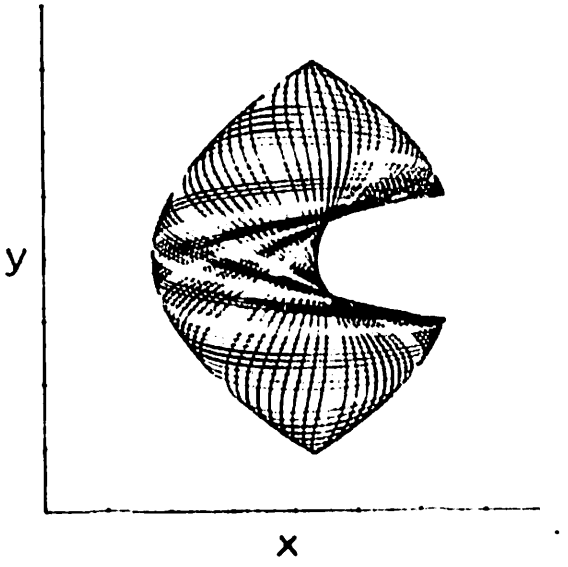

Fig.4 Trajectory for the Hamiltonian (2.2) for the Fermi-resonance case, $\omega_x = 2\omega_y$

We have extended this surface of section method to higher dimensions [11]. Whereas before we noted, say, the value of p_x and of x each time the trajectory crossed the y = 0 axis in a positive direction, now we note each time the value of xyz along the trajectory passes through zero, then collect the x = 0 cases and, for plotting p_z vs z, y occurring in the small interval $(-\varepsilon,\varepsilon)$, with $p_x > 0$, $p_y > 0$. In practice the phase integrals were evaluated in action-angle coordinates rather than conventional ones to reduce the number of points needed for the evaluation. The entire procedure was also applied to four-dimensional systems as well. The quantum mechanical energy eigenvalues were again evaluated by iteration, using (2.1).

A direct method for evaluating the quantum mechanical spectrum (differences of energy eigenvalues) from classical trajectories has also been developed here [12]: one computes an autocorrelation function such as $\langle x(0)x(t)\rangle$ from the trajectory, and takes the Fourier transform. A suitable form for the spectral function $I(\omega)$ which avoids the averaging over initial phases in $\langle\ \rangle$ was shown to be

$$I(\omega) = \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left\langle \left| \int_0^T x(t)\exp(-i\omega t)dt \right|^2 \right\rangle , \qquad (2.3)$$

where the remaining averaging now appears only in some statistical mechanical ensembles (e.g., a canonical one). An example of a spectrum for a finite trajectory time T is given in Fig.5 for the function $x(t)+y(t)$. The spectrum is seen to consist of sharp lines, as indeed it should in the quasi-periodic regime. Results comparing these semiclassical spectral lines with the quantum mechanical ones are given in [12] for this two-dimensional system. Analogous results were obtained for three-dimensional systems also [12].

In the "ergodic"[2] region the spectrum obtained by us was "broadened" under low resolution (cf [12], but with increasing length of trajectory time the spectrum

[2]Throughout this paper the term ergodic has been used somewhat loosely to mean a system reaching most of the energetically accessible phase space. It is still assumed that the time-average average equals the average over that space.

appears, increasingly, to consist of sharp lines.)

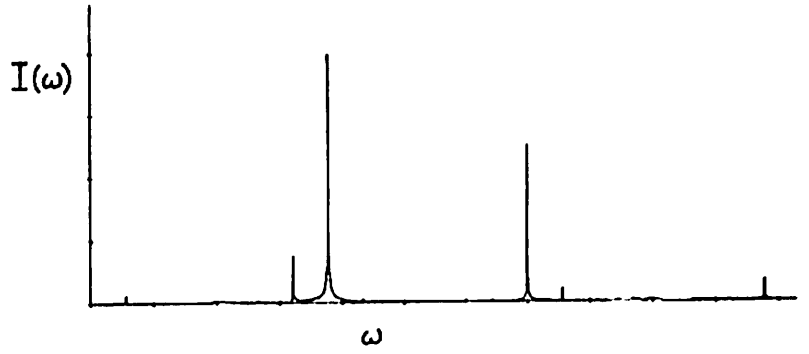

Fig.5 Power spectrum I(ω) of the function x(t) + y(t) for the case of two dimensions and the Hamiltonian (2.2), in the quasi-periodic regime

An example is given in Fig.6 for the system with the Hamiltonian (2.2) and at an energy for which one has exponential separation in time of neighboring trajectories. Three spectra are given, corresponding to three initial conditions at the same energy [11]. The trajectories for the spectra in Fig.6 were for long times, but nevertheless back integrated to two places (and conserved energy to seven places). Spectra for increasingly short times back integrated of course to more figures, but became increasingly less "structured." We have not yet run a spectrum which is a phase space average of these spectra. Unlike the quasi-periodic case the spectral intensities are approximately independent of the initial conditions at the given energy. The spectra are seen to consist of numerous "lines", perhaps evidence for CHIRIKOV's idea of overlapping resonances. (Resonances typically introduce additional lines.)

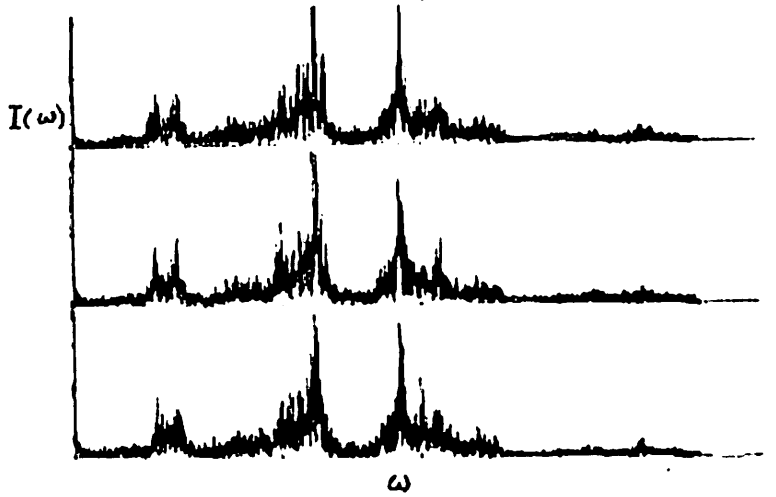

Fig.6 Legend as in Fig.5 but for the ergodic regime: the three spectra are for trajectories of a given energy but different initial condition

In the ergodic regime we find that trajectories at different initial conditions with the same total energy yield spectra which become increasingly similar the more the trajectories are able to average over all of phase space: If the trajectory has not been allowed sufficient time to pass through a large portion of phase space, the spectrum is still broad, and a longer trajectory would yield a somewhat different spectrum. Presumably the length of time needed for the spectrum in the "ergodic" regime to be independent of initial conditions at given energy is the recurrence time. Application of the spectral method to determine energy distribution of high energy molecules among various normal modes was made in a recent classical trajectory calculation [13].

3. Time-Dependent Problems

We consider here the motion of the atoms in a molecule under the influence of an oscillating electric field, a light pulse for example. The pulse may be coherent or incoherent. In either case the Hamiltonian for the motion of the molecule will depend on the coordinate q, the momenta p and, now, explicitly on the time t. One can show that the appropriate semiclassical wavefunction now for the time-dependent wave equation is again given by (1.1), but with S given by

$$S = \int_{q_0}^{q} p \cdot dq + p_0 q_0 - \int_0^t H \, dt, \tag{3.1}$$

and the P's now all being initial action variables. The average semiclassical value of, say, x(t), is given by

$$\langle x(t) \rangle_{sc} = \int |\psi(q,t)|^2 \, x \, dq, \tag{3.2}$$

where ψ is the semiclassical wavefunction,

$$\begin{aligned} \psi_{sc}(q,t) &= |\det \partial^2 S/\partial q \partial P| \exp(iS/\hbar) \\ &\equiv |\det \partial q_0/\partial q| \exp(iS/\hbar), \end{aligned} \tag{3.3}$$

where P denotes the initial action variables for this bound state system.

One can then show that the $\langle x(t) \rangle_{sc}$ in (3.2) is equal to its classical value,

$$\langle x(t) \rangle_c = \int_0^1 x(t) \, dq_0 \tag{3.4}$$

where the integration is over initial phases (initial angle variables) of the classical motion. I.e.,

$$\langle x(t) \rangle_{sc} = \langle x(t) \rangle_c \tag{3.5}$$

The conditions used to obtain (3.4) from (3.2) were (i) to neglect tunneling, if any, along the trajectory, i.e., to neglect the case where p in (3.1) is complex-valued over some portion of the path, and to consider the case where $\det|\partial q/\partial q_0|$ had no zeros. Remarks similar to those about x apply to any other functions of the q and p, such as that portion of the energy H_{mol} of the molecule not explicitly involving the oscillating electric field.

$$\langle H_{mol}(t) \rangle_{sc} = \langle H_{mol}(t) \rangle_c \tag{3.6}$$

The result (3.5) helps explain the similar behavior reported by Dr. Lamb at this conference, where he compared classical and quantum mechanical results for an oscillator in an oscillating electric field. As he suggested, one should compute $\langle x(t) \rangle_c$ by averaging over initial phases w_0, rather than begin with the oscillator classically at rest.

The derivation of Eq. (3.6) also provides some justification for the recent classical trajectory treatment of the behavior of a polyatomic molecule $CH_3C\ell$ under the influence of an intense oscillating electric field [14].

Further studies [15] utilizing these concepts are currently being performed in an attempt to characterize the effects of ergodicity on a classical calculation of infrared multiphoton disassociation.

4. Ergodic Wavefunctions

We have made both a classical trajectory study as well as a quantum mechanical variational calculation using the Hamiltonian (2.2) with $\omega_x = 2\omega_y$. At low energies the motion is quasi-periodic and trajectories which resemble curved rectangles are somewhat similar to those in Fig.4. The wavefunctions corresponding to a state in this energy region occupy a similarly shaped region of configuration space, as seen in Fig.7. At higher energies the classical motion becomes stochastic and the wavefunction occupies a correspondingly larger region of configuration space in Fig.8 [11]. Further aspects of this behavior are currently being examined [10].

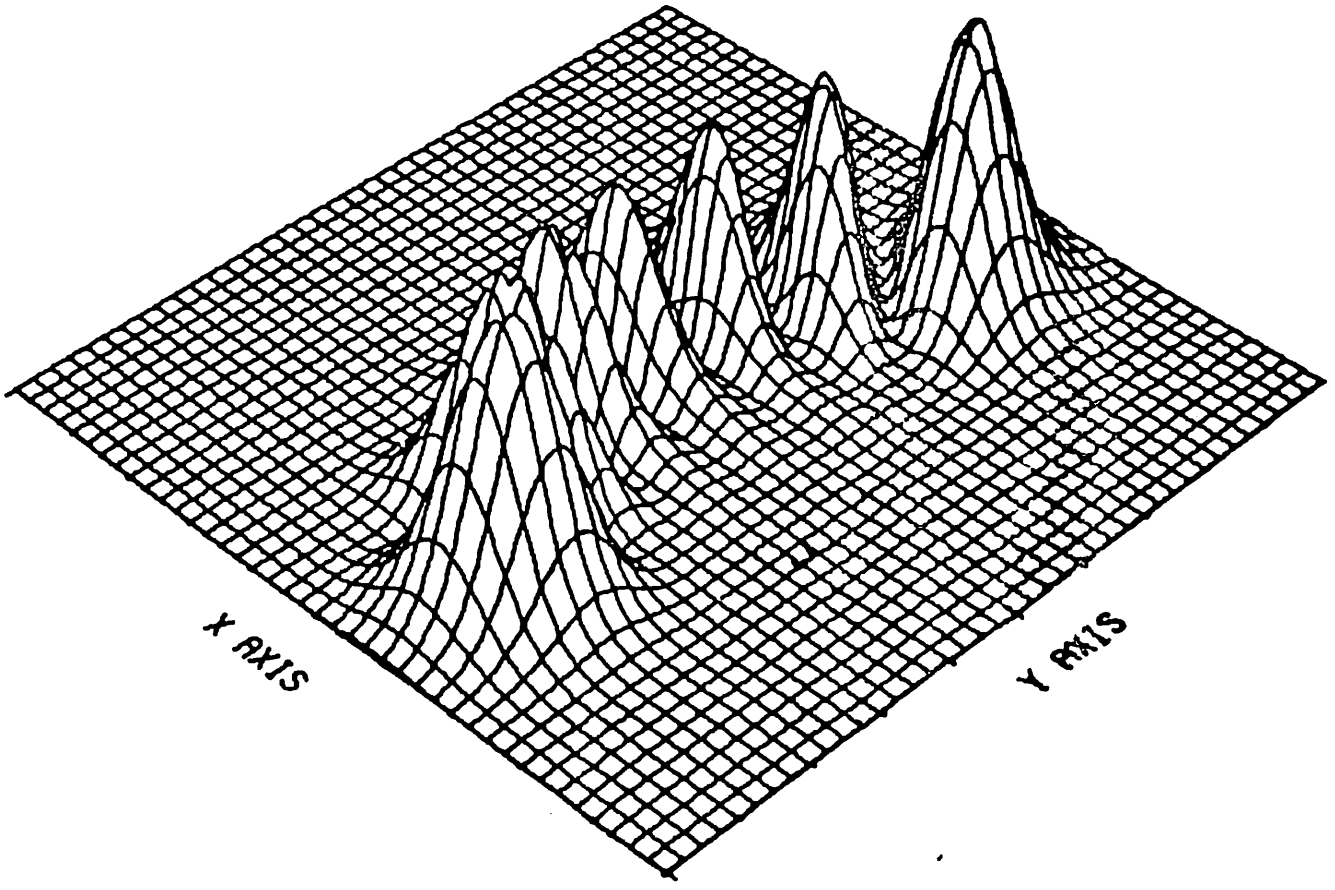

Fig.7 A wave function for the Hamiltonian (2.2) at an energy where the classical motion is quasi-periodic, for the Fermi-resonance case

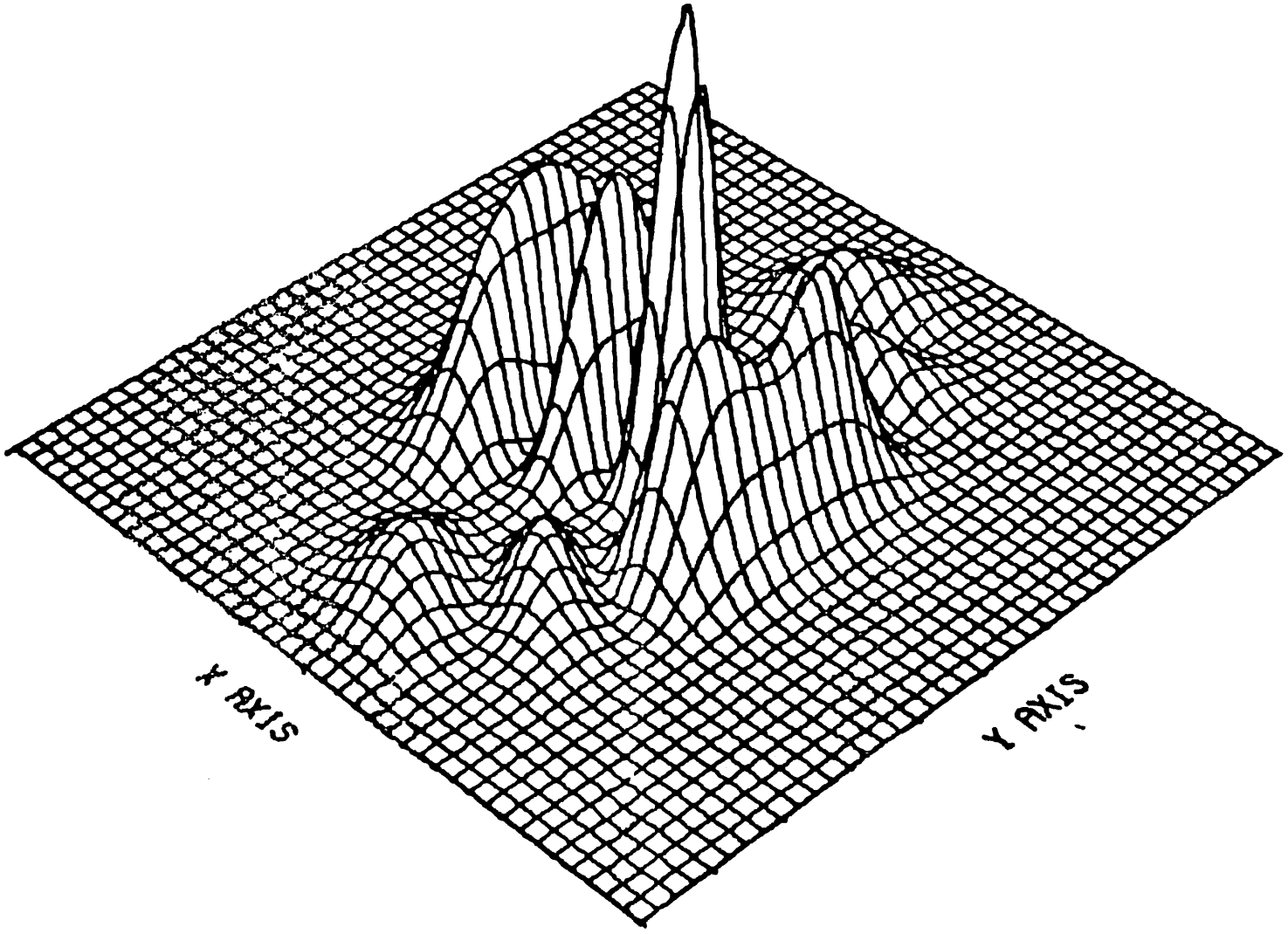

Fig.8 Legend as in Fig.7, but for the case that the classical motion is "ergodic"

Additional studies [16] using a numerical integration of the time-dependent Schrodinger equation for a system in the presence of an external laser field have been done at various values of the laser power and frequency. The wave functions have been observed to change from a localized type to one spread out with many ripples, after the system has absorbed sufficient energy from the field.

5. Concluding Remarks

In the present paper we have surveyed some recent results of semiclassical theory of anharmonic systems. The results draw on some of the classical concepts being treated at this conference.

TABLE I

Comparison of the semiclassical and quantum energy levels for various systems

System ω_x^2, ω_y^2 λ, η	Quantum numbers (n_x,n_y)	Eigenvalues Quantum	Semicl.	Uncoupled $\lambda = 0$
0.29375, 2.12581,	0,0	0.9916	0.9920	1.0000
	1,0	1.5159	1.5164	1.5420
-0.1116, 0.08414	2,0	2.0308	2.0313	2.0840
	0,1	2.4188	2.4198	2.4580
0.36, 1.96	0,0	0.9939	0.9942	1.0000
-0.1, 0.1	1,0	1.5809	1.5812	1.6000
	2,0	2.1612	2.1616	2.2000
0.49, 1.69	0,0	0.9955	0.9954	1.0000
	1,0	1.6870	1.6870	1.7000
-0.1, 0.1	0,1	2.2781	2.2785	2.3000
	2,0	2.3750	2.3751	2.4000
	1,1	2.9583	2.9588	3.0000
	0,2	3.5479	3.5480	3.6000
0.81, 1.21	0,0	0.9980	0.9978	1.0000
	1,0	1.8944	1.8944	1.9000
-0.08, 0.1	0,1	2.0890	2.0889	2.1000
	2,0	2.7899	2.7900	2.8000

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