Ann. Rev. Phys. Chem. 1981. 32:267–309

QUASIPERIODIC AND STOCHASTIC BEHAVIOR IN MOLECULES[1]

*2730

D. W. Noid

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

M. L. Koszykowski

Sandia National Laboratories, Livermore, California 94550

R. A. Marcus

California Institute of Technology, Pasadena, California 91125

INTRODUCTION

The extent and rate of intramolecular energy transfer play a role in a variety of problems in chemical dynamics. Examples are unimolecular reactions (1a,b), chemical activation (2a,b), vibrational-rotational-translation energy distribution of the products of a dissociating species (3, 4), infrared multiphoton decomposition of molecules (5a,b, 6), internal conversion and intersystem crossing of electronically excited states (7a–d), dissociation of vibrationally excited state-selected van der Waals complexes (8), fluorescence spectra of electronically and vibrationally excited molecules (9a,b, 10a,b), chemiluminescent spectra of vibrationally excited molecules (11), reactions induced by excitation of high overtones of a bond vibration (12a–c), and high overtone spectra (13a,b). The present article reviews recent theoretical studies on the quasiperiodic and chaotic dynamical aspects of vibrational states and describes how those studies may be related to intramolecular randomization.

In the earliest of these phenomena extensively studied, that of unimolecular reactions, two limiting forms of a theory of unimolecular dynamics were given some decades ago—RRKM (Rice, Ramsperger, Kassel, Marcus) (1, 14) and Slater theories (15). The first assumes, in effect, that the molecule can explore all of the energetically accessible phase space available to it, consistent with the given total angular momentum and the given energy. The second assumes, instead, that there are, in addition, hidden constants of the motion which further limit the region of phase space explored by the molecule. For example, in the Slater theory normal modes of vibration (harmonic oscillators) are assumed in these quite anharmonic molecules, and so the assumed constants of the vibrational motion are the maximum amplitudes of each normal mode during the motion of the isolated molecule.

Most of the current experimental evidence on unimolecular reactions supports the first approach (sometimes termed the statistical approach) (1a,b). However, in some cases, such as in the excitation of a van der Waals complex (8) to a vibrational state v of the molecular part, and the subsequent dissociation, e.g.

$$I_2He + h\nu \rightarrow I_2^*(v)He \rightarrow I_2^*(v-1) + He,$$

dissociation occurs before the molecules can randomize its energy among the various coordinates.

In RRKM theory it is assumed that intramolecular energy randomization is complete before dissociation or isomerization occurs. The time for the dissociation (isomerization) depends on the molecule and on its vibrational energy but is frequently of the order of nanoseconds. An example where the actual time for randomization has been estimated in experiment, namely by Rynbrandt & Rabinovitch (16), involves the reaction

$$CF_2(CD_2)CF-CF=CF_2 + CH_2 \rightarrow CF_2(CD_2)CF-CF(CH_2)CF_2,$$

where the CH_2 containing ring is, thereby, formed in an initially vibrationally excited state. The estimated time for intramolecular ring-to-ring energy transfer from the experiments was about 1 ps. Analogous times for other intramolecular energy transfers were estimated in other chemical activation experiments (17).

The study of dissociation, chemically activated or multiple infrared photon induced, under collision-free conditions in molecular beams (6), plus related studies in low pressure bulb systems (17), are of particular interest. For example, it has occasionally been suggested that "intramolecular" randomization is due to long-range collisions, a possibility which, it has been argued, has been eliminated in suitable studies (17a,b, 18).

The question of how intramolecular energy transfer occurs is perhaps obvious on a classical basis but is a more subtle one quantum mechanically, and we consider it below. There is, for example, no "intramolecular energy randomization" if the state of the vibrationally excited molecule prepared by collision or by IR or UV light absorption were a single stationary quantum state.[2] The excitation step in intramolecular energy randomization experiments then involves the preparation of a group of states, and recognition of this is important in understanding randomization.

Studies of the nature of the underlying anharmonic motion are expected to provide added insight into the various experiments related to the intramolecular energy transfer, and to provide understanding for the nature and meaning of "randomization." This article on recent theoretical work—classical, quantum, and semiclassical—is divided into a number of parts. In the first, we review the classical mechanical developments in anharmonic systems (as molecules are). There is numerical and theoretical evidence on the nature of vibrations. Notably, the famous KAM (Kolmogorov, Arnol'd, Moser) theorem (19–23), which dates from the middle 1950s and early 1960s, states that at sufficiently low perturbations (and thereby by a scaling argument at low energies) the classical motion of a system of coupled anharmonic oscillators is largely quasiperiodic ("regular"), i.e. has good action variables (19–23). At higher energies, for an increasing fraction of initial conditions, it tends to be "chaotic" though deterministic. [The former corresponds to an anharmonic version (24) of Slater's theory while the latter corresponds to RRKM-type theory, as discussed below.] Theories exist for the prediction of the energy range where this largely chaotic motion becomes important, and these too are considered. The various ways in which regular and chaotic motion is usually detected numerically are also summarized.

In the second and third parts of this article we review the question of possible analogous semiclassical and quantum mechanical behavior. Many methods are now available for calculating quantum mechanical eigenvalues in the "regular" regime from classical mechanics using semiclassical arguments. This aspect of the quantum mechanics of bound states is reasonably well understood and is reviewed first. Semiclassical efforts to make calculations of eigenvalues in the chaotic regime are less well-founded theoretically but are also examined. Current results to date in the chaotic regime depend mainly, though not exclusively, on the use of perturbation theory, which assumes the system to have good action vari-

[2]Except in the case of a "chaotic" quantum state, described below. In this case, the "randomization," as judged by the probability density $|\psi|^2$, is instantaneous: The pure state excited is already a "randomized" state.

ables, i.e. by definition to be quasiperiodic even when it is largely chaotic, i.e. even when the good action variables do not exist.

Various alternative suggestions have been made as to what constitutes analogous regular and chaotic quantum mechanical behavior, and these are compared. We consider in a later section the ways in which this difference in behavior may or may not be revealed in experimental observations.

The fourth part contains a review of related work on spectral properties, including the calculation of a classical power spectrum from a classical trajectory, a comparison with the aid of semiclassical ideas with the quantum mechanical power spectrum of the same variable, and some discussion of local versus nonlocal modes of vibration.

We cite in the fifth part some recent classical trajectory studies. Applications of techniques and phenomena discussed in the previous sections are also presented. Direct experimental data on intramolecular energy transfer are sparse, but we do cite some indirect data. Major questions remain to be resolved both experimentally and theoretically, and some of these are noted. Not surprisingly, a number of uncertainties or controversies exist in this relatively young field, and we address some of these too.

There is a substantial body of literature on model or formal descriptions of radiationless transitions (7) and, increasingly, of infrared multiphoton absorption. It would be interesting to relate such studies to the notion of quasiperiodic and chaotic states discussed in the present article; however, some brief remarks are made.

The literature reviewed in this article is primarily that prior to December 1980, although in several cases it was possible to include later papers.

CLASSICAL MECHANICS

The classical mechanics of Hamiltonian systems of coupled oscillators (and hence of vibrating molecules) has been the subject of intense study in recent years (19–23). During this period the conceptual understanding of the detailed as well as of the qualitative dynamics has undergone a radical transformation. The framework for the study of the dynamics of nonlinear systems originated in the seventeenth century with the development of classical mechanics. Cases for which a separation of variables can be made do not reflect the actual dynamics of highly coupled systems or of weakly coupled highly energetic systems. Approximate methods (25a,b) were developed to study coupled systems and have proven to be useful in many cases; however, they explicitly excluded any possibility of detecting fundamental changes in the underlying dynamics—which is the central theme of this review. Around the turn of the century there was specula-

tion by Poincaré (26) that systems with extremely different types of dynamics could exist. Nowadays, it is commonly accepted that three different regimes of the dynamics exist: (*a*) a regime where the classical motion is largely quasiperiodic, (*b*), a mixed regime of quasiperiodic and chaotic motion at different initial conditions, and (*c*) a regime of largely chaotic motion.

The advent of digital computers made possible "exact" calculations of the motion of coupled systems. The classic first study was by Fermi et al (27), published in the 1950s, and involved an exact numerical solution of the equations of motion for a linear string of anharmonically coupled oscillators. Some years later there was renewed interest in the field and several groups of astronomers (e.g. 28–30a,b) demonstrated that two coupled oscillators could exhibit regimes of qualitatively different dynamics. This work was later reproduced by many groups using more accurate numerical methods. The KAM theorem states that quasiperiodic motion will occur for extremely small values of the perturbation. There is numerical evidence that it also occurs at larger perturbations and that at still larger ones some qualitative transition in the nature of the classical dynamics may occur.

The classical motion is of two types. The first type of motion, which is similar to that observed in uncoupled systems, is called by various authors quasiperiodic, regular, or stable. The second type of motion, which is qualitatively different from the first, has been loosely but equivalently referred to as chaotic, stochastic, ergodic, or irregular. Such a classification for classical dynamics has implications for a wide range of disciplines, such as chemical kinetics (1), laser chemistry (5, 6), high resolution spectroscopy (31a,b), lattice dynamics (32), plasma physics (33), astronomy (28–30a,b), and fluid mechanics (34). Examples of several trajectories of the quasiperiodic type are given in Figures 1–3. An example of a chaotic type of trajectory is given in Figure 4.

At least six different features distinguish the two types of motion. They are described below:

1. One difference is the behavior of a trajectory in occupying phase space. A trajectory is defined as the set of coordinates $\mathbf{q}$ and their conjugate momenta $\mathbf{p}$ as functions of time which result from the solutions of Hamilton's equations for a given set of initial conditions. When a $2m$ dimensional phase space (m is the number of coupled vibrations) is divided into volume elements, the quasiperiodic trajectory will occupy only a limited number of the energetically allowed elements, while the chaotic trajectory appears to occupy all or almost all of them. In the quasiperiodic case the trajectory covers ergodically a manifold (a torus) of at most m dimensions in the phase space (20), and so the constants of the motion are

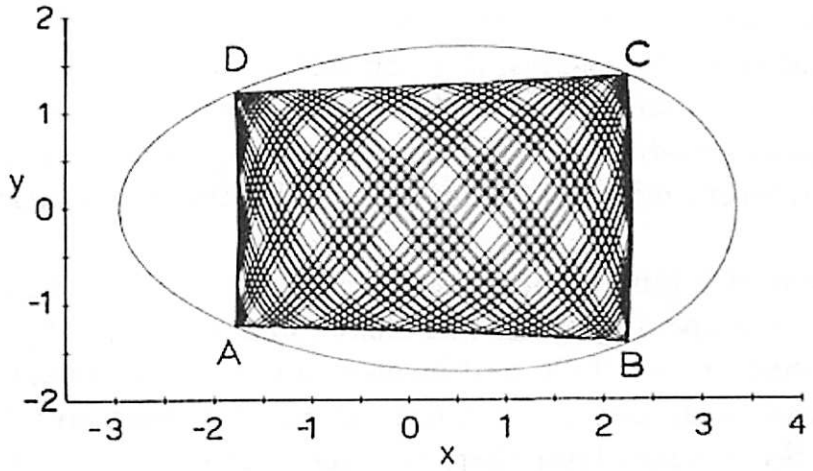

Figure 1 A plot of a quasiperiodic trajectory for the Hamiltonian,

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

with ω_x and ω_y incommensurate: $y(t)$ is plotted versus $x(t)$. The trajectory is bounded by the "caustics" AB, BC, CD, and DA. On the ellipse-like curve the potential energy equals the total energy.

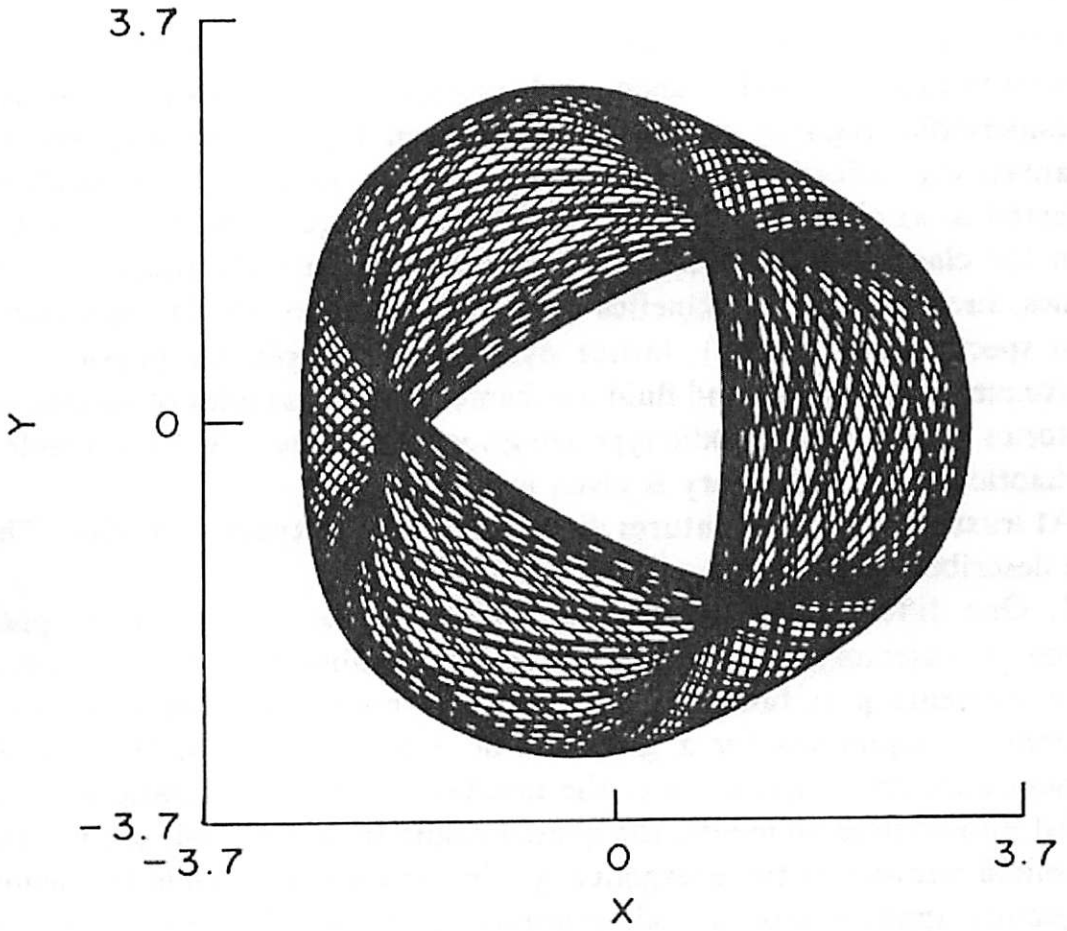

Figure 2 A plot of a quasiperiodic trajectory for the Hamiltonian given in the legend to Figure 1, with $\omega_x = \omega_y$.

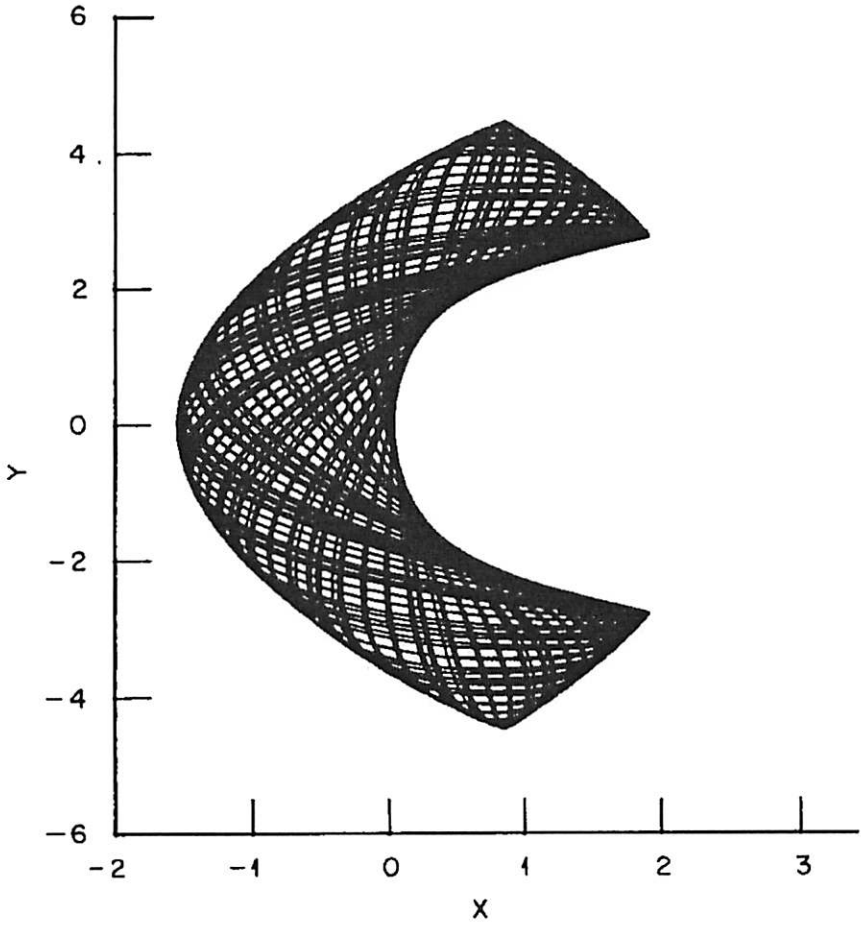

Figure 3 A plot of a quasiperiodic trajectory for the Hamilton given in the legend to Figure 1, with $\omega_x = 2\omega_y$.

of a type which restrict its coverage of phase space considerably. The property of the filling of phase space by a chaotic motion can most easily be seen by examining a projection of the trajectory onto a plane in the $2m$-dimensional phase space. The plane for $m = 2$ could be chosen as $q_1 = 0$, $p_1 > 0$ and thereby one plots p_2 vs q_2. These plots, known as Poincaré surfaces of section, are widely used to examine the dynamics of coupled oscillators (28–30a,b). A quasiperiodic surface of section will appear to be a smooth closed curve (the projection of the torus on the $p_2 - q_2$ plane). A chaotic surface of section will consist of points that appear to be randomly scattered over the energetically accessible region of the plane. These Poincaré surfaces of section can be extended to higher dimensions, as noted below. An example of a Poincaré surface of section for several quasiperiodic trajectories is given in Figure 5.

2. The apparent randomization of some phase space trajectories leads naturally to the speculation that a comparison of microcanonical phase space and time averages of some function of the dynamical variables would also be a useful criterion. The averages would not be the same in

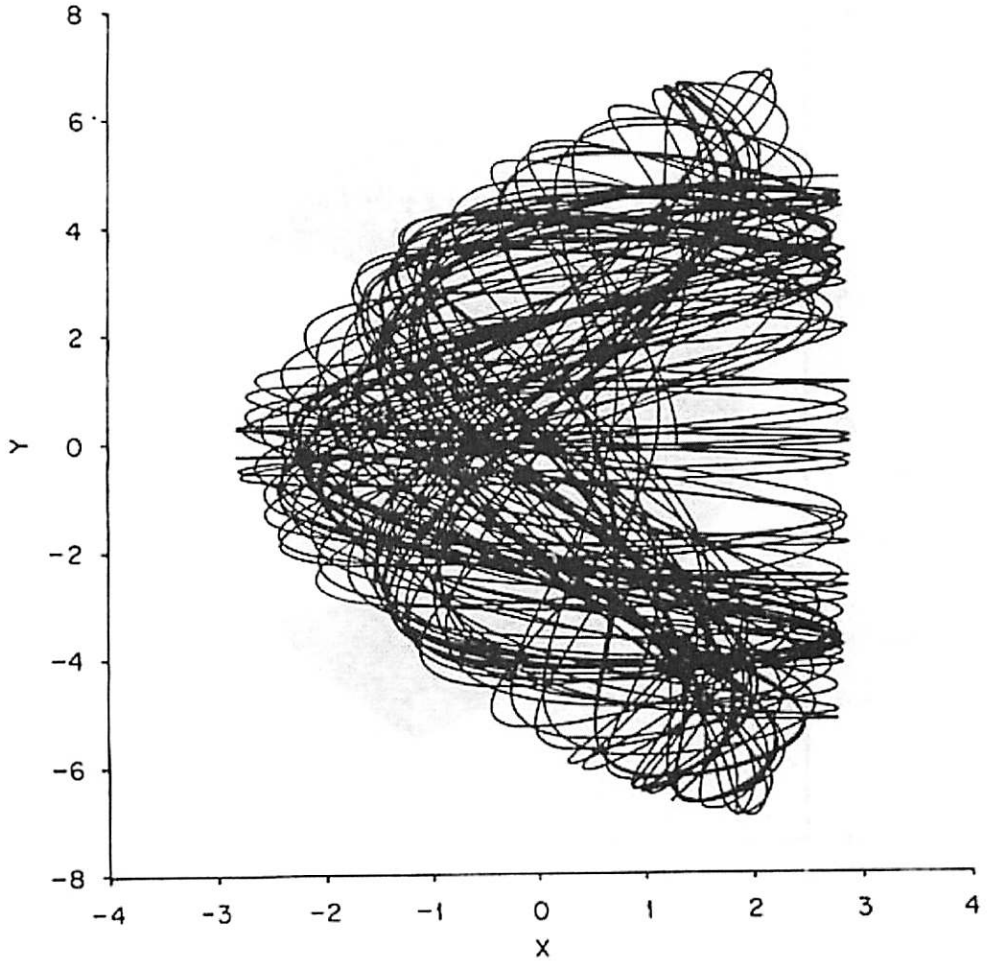

Figure 4 A plot of a chaotic trajectory for the system in Figure 3 but computed for a higher energy.

the quasiperiodic case, but in the chaotic regime they are expected to be the same or nearly the same. The equivalence of time and phase space averages is the basic assumption of the quasi-ergodic hypothesis of statistical mechanics (35). It was thought that a large number of degrees of freedom were necessary for this hypothesis to be correct but now one finds this chaotic behavior in systems with as few as two degrees of freedom.

3. Another method of differentiating the two types of classical motion, introduced by Noid et al (36), involves looking at the frequency spectrum of a dynamical variable or correlation function for a trajectory or for a set of trajectories (36–40),[3]

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty} \langle f(0)f(t)\rangle e^{-i\omega t}\,dt \qquad 1.$$

$$= \frac{1}{2\pi}\lim_{T\to\infty}\frac{1}{T}\left|\int_{-T}^{T} f(t)\,e^{-i\omega t}\,dt\right|^2, \qquad 2.$$

[3]The derivation of Eq. 2 from Eq. 1 is given in (36).

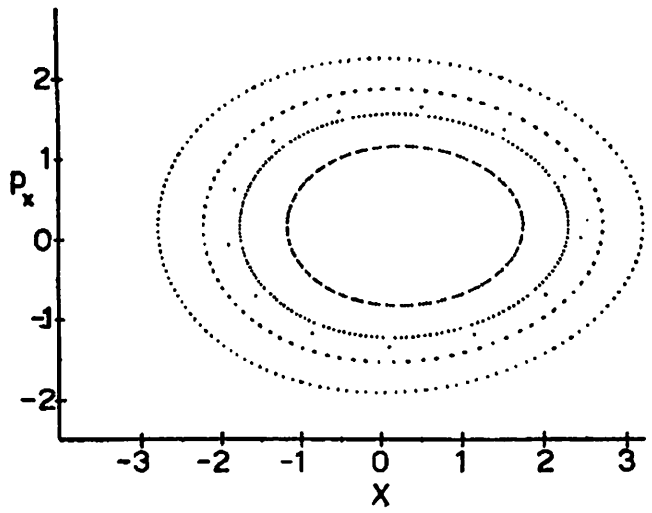

Figure 5 A Poincaré surface of section for five different trajectories of the type depicted in Figure 1. One is a periodic trajectory (13 dots).

where $f(t)$ is any function of the coordinates and momenta. To obtain a classical infrared absorption spectrum one sets f to be the dipole moment. The $\langle\ \rangle$ indicate an average over the appropriate ensemble of trajectories. It is, in Eq. 1, an average over trajectories having the same action variable, but different angle variables, i.e. phases. In Eq. 2, in the quasiperiodic (but "non-degenerate") case, a single trajectory suffices to obtain the spectrum corresponding to a torus. (In a degenerate system a family of rotated trajectories describes a torus.) The frequency spectrum of a dynamical variable for quasiperiodic motion consists of a series of sharp lines, the m fundamentals for m coordinates, the overtones, and combinations. The chaotic frequency spectrum has a broad series of lines forming, perhaps, a continuous band if the trajectory time is infinite. The bands occur near the sharp lines of any neighboring quasiperiodic trajectory. Examples of a spectrum for a quasiperiodic trajectory and for a chaotic trajectory are given in Figures 6 and 7.

4. The correlation function of a dynamical variable changes from being flat or oscillatory (totally correlated) in the quasiperiodic regime to decaying (uncorrelated) in the chaotic regime (41). When the energy is placed in some zeroth order mode initially for any trajectory, that modal energy undergoes regular oscillations in the quasiperiodic regime but decays intramolecularly in the chaotic regime [apart from Poincaré recurrences (42) in the latter case] (41). This method is closely related to No. 3.

5. The motion of two neighboring points in phase space has very often been used in numerical experiments to distinguish between the two types of motion. Quasiperiodic motion is characterized by a linear separation of

the points, while for chaotic motion the points separate exponentially (43a,b, 44).

6. Property 5 led Kolmogorov (45) to define an entropy of the trajectory which has been found to change fairly rapidly at a critical energy where the dynamics change from largely quasiperiodic to largely chaotic. In practice one does not numerically calculate the Kolmogorov entropy but rather an approximation to it called the k-entropy or an entropy-like quantity. The latter is defined as (46a–c)

$$k = \lim_{n\to\infty} \frac{1}{n\tau} \sum_{i=1}^{n} \ln \frac{|d_i|}{|d_0|} \qquad 3.$$

where $|d_0|$ is the initial separation between two trajectories. The $|d_i|$ are defined as follows: $|d_1|$ is the separation at time τ. The trajectories are then "slid" a distance $|d_0|$ apart again and integrated a time τ to produce a separation distance $|d_2|$. The process is repeated until Eq. 3 converges. Benettin et al (46a,b) have calculated the k-entropy for some systems,

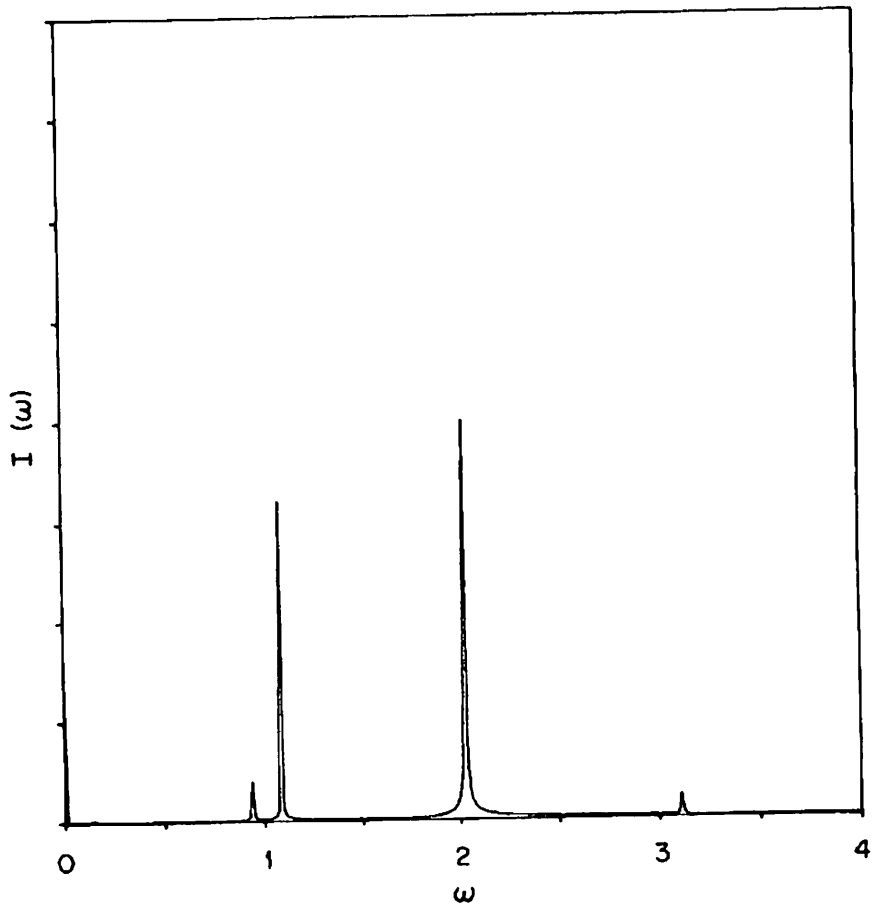

Figure 6 A power spectrum of the variable $x + y$ for a quasiperiodic trajectory similar in shape ("box-like") to the one in Figure 1. The intensity $I(\omega)$ at frequency ω is plotted versus ω. The width of each line is due to a truncation error which could be reduced in size by using longer time trajectories.

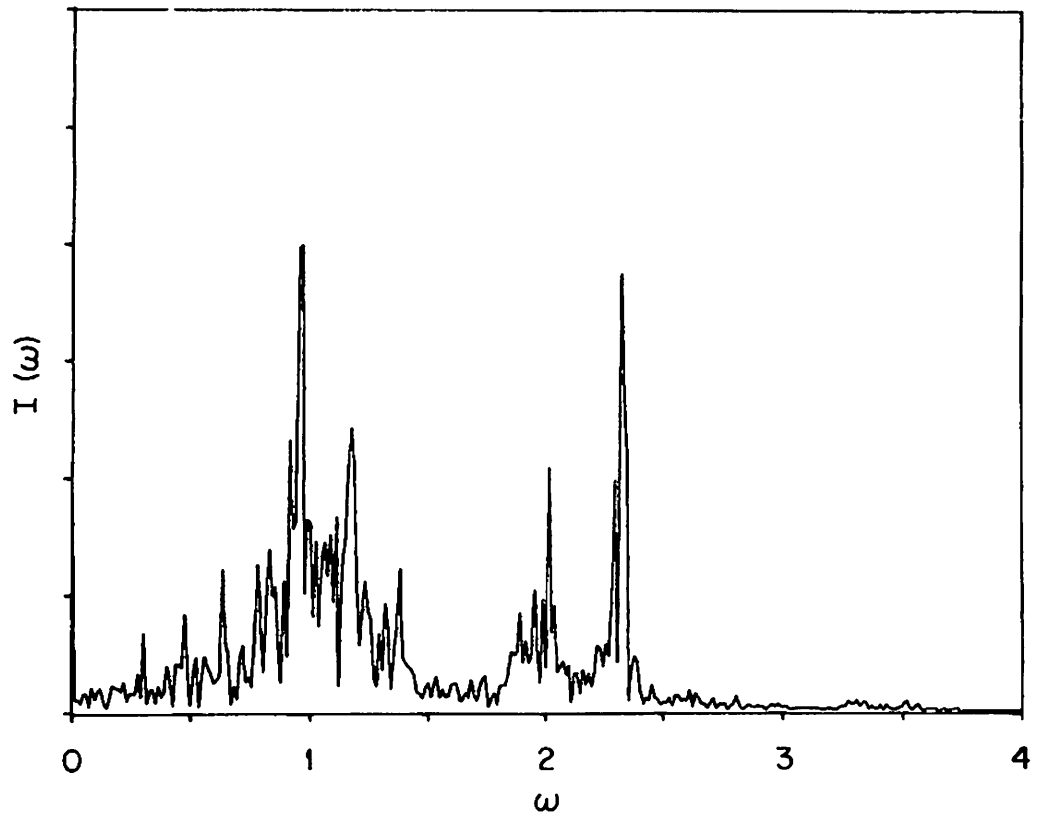

Figure 7 The power spectrum described in the legend to Figure 6, but for the chaotic trajectory in Figure 4.

and in particular for the Hénon-Heiles (28) system, and discussed the relation to the Kolmogorov entropy.

The transition from predominantly quasiperiodic to predominantly chaotic motion arises when one has added enough energy to the system, or alternatively, when the coupling parameters have been increased. The critical value of the energy or of a coupling constant in the Hamiltonian is usually obtained with numerical experiments, but it has also been studied with various approximate analytical methods. As with all approximate methods, the selection of a zeroth order Hamiltonian is crucial to the success of each method. No method presently exists for predicting whether or not a system is "integrable," i.e. quasiperiodic for all initial conditions. Several of the methods designed to predict the critical energy are briefly described below.

The earliest of these methods, called the overlap of resonances method, is due to Chirikov (47a–c) and to Ford (43a,b). In this method the Hamiltonian is written in terms of zeroth order action-angle variables and the coupling is expanded in a Fourier series. When there exist a large number of periodic terms ("resonances") which resonantly couple the oscillators in a perturbative treatment, one predicts that the motion will be chaotic.

Detailed studies have found that this approach leads to qualitative agreement with numerical experiments. As stated earlier, the prediction depends upon the selection of the zeroth order Hamiltonian. This method has been applied to coupled oscillators (e.g. 48a,b, 49). Using Chirikov's method, Oxtoby & Rice (49) obtained good agreement with the trajectory studies of Bunker (50) for predicting the onset of stochastic (RRKM) behavior for a number of systems.

Toda (51) and Brumer & Duff (52a,b) have devised another approach (TBD) which has had some success and has been recently modified by Cerjan & Reinhardt (53). This TBD approach associates chaotic motion with negative curvature in the potential energy surface. If the trajectory can reach such a point of negative curvature, the motion is predicted to be chaotic. Limitations of this approach have been described (48, 54–56). Aizawa (55) has performed detailed numerical experiments on the Hénon-Heiles Hamiltonian and shown for this system that the regions of negative curvature are not related to the chaotic motion.

Another method, due to Mo (57, 58), consists of calculating the phase space averaged time correlation function of some dynamical variable. This calculation is approximate and uses techniques developed by Mori & Zwanzig (59a,b). It seemed to be successful for several model systems. The prediction of chaos rested on calculation of the moments. An exact calculation of the moments (41) for the Hénon-Heiles Hamiltonian has shown them to vary smoothly with energy (rather than abruptly) and to differ by about 15% from those calculated perturbatively (57), yielding a corresponding modification of the predicted critical energy for onset of chaos (60). However, the basis of Mo's method, namely the change of a correlation function with energy, is presently questionable, since no obvious break in behavior from oscillatory to exponential was observed (41).

Ramaswamy & Marcus (61) have given a graphical method of locating the centers of resonances. They used a perturbative method to calculate the energy, for a fine uniform grid of action variables. The energy was plotted vs a parameter in the Hamiltonian and they looked for intersections. At such intersections (in the limit of a sufficiently fine grid) the derivative of the energy with respect to some action variable vanishes, i.e. there is a resonant center. One could then use Ford's method (43a,b) to calculate resonance widths and look for overlap of resonances. Another graphical method, in the form of modal energy plots, for describing resonant interaction regions has been given by Oxtoby & Rice (49).

We outline in this section the main features of classical motion in the quasiperiodic and chaotic regimes. There are, of course, many factors which complicate an understanding of Hamiltonian dynamics. It has been demonstrated that different regions of quasiperiodic and chaotic motion

can exist at the same energy. Systems with sufficient energy to escape can also be found to exhibit quasiperiodic motion, and therefore never escape. The nature of the complications of a system with three coupled oscillators is still controversial: It is not yet clear whether at a given energy the multidimensional phase space can be divided into two (chaotic and quasiperiodic) regions or whether there are instead different "chaotic" trajectories with different average properties (62a,b, 63a,b).

In this section we discuss only, and that briefly, Hamiltonian systems with smooth potentials. More details and discussions of hard potentials and algebraic mappings are given in the recent reviews of Tabor (64) and Berry (65).

SEMICLASSICAL EIGENVALUES

The discussion in the previous section indicates that two types of dynamics will be important in anharmonic systems. As a first step toward understanding the semiclassical dynamics of isolated molecules we consider next systems of relatively low energies, i.e. in the quasiperiodic regime. The semiclassical analysis to be used seeks a correspondence between this classical dynamics and the quantum mechanics. Semiclassical mechanics has its beginning in the old quantum theory (Eq. 4) (66) developed by Bohr, Sommerfeld, Einstein (67), and others:

$$\oint_{C_i} \sum pdq = (n_i + \delta_i)\, 2\pi\hbar, \quad (i = 1 \text{ to } m) \qquad 4.$$

where the $\mathbf{p}$ and $\mathbf{q}$ are $2m$ conjugate momenta and coordinates, the n_i are quantum numbers, the C_i are topologically independent paths, and δ_i are known constants whose values were obtained for various systems by Keller (68a,b) and Maslov (69). A perturbation series for the action variables was used by Born (66) for treating systems having smooth potentials. "Old quantum theory," now in the form of semiclassical wave mechanics, was later extensively applied to obtain quantitative results for systems with hard-wall potentials by Keller (68a,b). More recently, Marcus and co-workers (56, 70–74) were able to obtain bound state eigenvalues for nonseparable anharmonic systems with smoothly varying potentials. In the following discussions we describe the recent methods as exact, iterative (which would be exact if converged), or noniterative.

The first exact technique used classical trajectories and was introduced by Eastes & Marcus (71). They calculated the topologically independent $\oint \Sigma pdq$ integrals along the caustics (the multidimensional classical "turning points"). (The caustics are indicated in Figure 1, AB, BC, CD, DA.) The initial conditions of the trajectory were then varied until one trajec-

tory was found that gave integer values for the quantum numbers n_i for Eq. 4. The agreement with a quantum calculation for a system of two coupled oscillators with noncommensurate frequencies was excellent. This technique is difficult to apply when the caustic has a complicated structure, and the method was extended by Noid & Marcus (72). Instead of caustics, Poincaré surfaces of section were used for the paths C_i to evaluate the integral in Eq. 4. The surface of section technique, which is computationally much simpler than the caustic method, was applied (72) to the same system used earlier and the results were in excellent agreement, as they should be. The surface of section technique was also successful in calculating eigenvalues for a state where the caustics underwent radical changes (for the "box-like" (71) or nonbox-like trajectory cases). The method was also applied to systems with 1:1 (73) and 1:2 (56) resonances in the zeroth order problem, again with reasonably good agreement with an exact quantum calculation. By using the surfaces of section expressed in terms of zeroth order action angle variables, it was possible to extend the method to give excellent results for a three dimensional system (74). The modified method was computationally simpler than the previous one. The energies of compound state resonances have also been found with this method by quantizing quasibound trajectories (75). The system studied had a Morse-harmonic potential with parameters chosen to resemble a colinear collision of an inert gas atom with a diatom halogen (75).

There are a number of approximate semiclassical quantization techniques. They range from relatively simple noniterative approximate procedures to iterative perturbative methods. Each method implicitly assumes that a torus or "remnant of a torus" exists. (The torus itself does not exist in the chaotic regime.) For some cases the approximate methods tacitly assume that the shape of the torus is only a minor distortion from that of the unperturbed torus. Direct information on the shape of the torus, when it exists, is provided by the exact trajectory method described above. It permits one, for example, to adapt the choice of Poincaré surface of section to this shape (e.g. by using various curvilinear coordinates). The methods are thus complementary.

Percival & Pomphrey (76a–c, 77) have developed two closely related methods based upon a classical variational principle for motion on a torus. In the one they most commonly use, the time-dependent classical variables are expanded in a Fourier series. Frequencies are chosen, Fourier coefficients are evaluated numerically, and the process is iterated. The equations were, as in all of classical mechanics, obtained from a variational principle, but the method appears to be iterative rather than variational in the usual sense. These authors have also developed a variational method (76a–c, 77) in which a trial expression for the energy was chosen,

obtained for example from a low order perturbation theory, and the parameters were evaluated by finding the minimum energy for the given action variables. The latter has been applied to the helium atom (78a,b).

The first (iterative) procedure (76a–c, 77) is iterated to make the value for the energy converge for integer quantum numbers and thus provide the semiclassical eigenvalues. The method yielded excellent agreement with exact quantum results for several two and three dimensional nondegenerate systems, for those eigenvalues for which convergence was obtained. Jaffé & Reinhardt (79) recently applied the method to a nearly degenerate system and to a very energetic system and found that for some states it diverged. Colwell (80) used an admittedly ad hoc method to remove this difficulty. She omitted the terms in the Fourier expansion that caused the divergence. This modification yielded a number of eigenvalues for OCS not obtained by the original procedure (77), but, as Colwell has remarked, without analytic justification. Approximately 70% of the bound state eigenvalues for OCS could be obtained in this way (80).

Chapman et al (81) have developed an iterative method which is an extension of Born's perturbation approach (66), by use of iteration on the generating function. The generating function is expanded in a Fourier series (as it can be for tori when they exist) and the series is truncated. Real as well as complex Fourier series have been used in the application of this method to two-dimensional model systems as well as to SO_2 and H_2O (82). All were in good agreement with quantum mechanical calculations. The method has not been used for degenerate systems thus far.

Sorbie & Handy (83–86) have developed an approximate perturbative noniterative method based upon classical trajectories. This method, based upon evaluating the $\oint pdq$ over a trajectory until it "closes" or comes arbitrarily close to closing upon itself, probably works best if the trajectory is box-like and hence for a nondegenerate system. Model systems (84) as well as nonrotating H_2O and SO_2 have been treated by this method (85). The computational time may be comparable to that of the "exact" surface of section technique.

Delos & Swimm (87a–c) have applied a perturbative noniterative method to a nonseparable anharmonic classical system by using a method developed by Birkhoff (88) and Gustavson (89). Basically the method is a procedure to canonically transform the Hamiltonian into a power series in harmonic oscillator Hamiltonians. Like all perturbative expansions, the expansion used in general ultimately diverges (90a–c) and one must truncate. For example, Contopoulos (63a) reported results on a model system using second, eighth, and eleventh order perturbation theory. Eighth was better than second but eleventh diverged. Delos & Swimm truncated the expansion at eighth-order and the resulting Hamiltonian of uncoupled

new harmonic oscillators was quantized via the usual semiclassical path integrals. The method was applied to a model two-dimensional system with no degeneracies and was found to give excellent agreement with a quantum calculation. When applied to a system with 1:1 zeroth order degeneracy the agreement was not as good: ~87% of the quasiperiodic and 60% of the eigenvalues in the classically chaotic regime were reported (87a–c). It should be pointed out, however, that this is the first method discussed to obtain eigenvalues when the classical dynamics was chaotic.

Jaffé & Reinhardt (79) have devised a perturbative noniterative method which is most closely related to that of (81). While Chapman et al (81) expanded the canonical transformation to the good action variables in a series, Jaffé & Reinhardt used a series of canonical transformations to obtain the good action variables, which they described as the classical limit of the Van Vleck transformation. They calculated action-angle variables to zeroth order, then to first order, etc. This iteration was continued until the action variables seemed to converge. Good agreement was obtained for several model systems with two degrees of freedom (79), and for most states in the Hénon-Heiles system for the perturbation parameter used (91).

The computer algorithms for the perturbative-iterative and variational methods are lengthier than that of the trajectory-surface of section method, but typically require less computer time, at least for systems with polynomial potentials. The main limitation of the former involves convergence.

Schatz and co-workers (92, 93) have also developed techniques based upon Born's perturbation theory. These involve using either a second order perturbation calculation or using classical trajectories to evaluate a quantum number as the phase average of the unperturbed quantum number over the trajectory. This second method tacitly assumes that the trajectory is box-like and that the caustics are only slightly distorted from the unperturbed ones. They have calculated eigenvalues for several nondegenerate model systems and for the stretching vibrations of CO_2 and have obtained good agreement with the quantum values (92). This work has also been applied to scattering calculations (93): the method was used to determine the initial conditions for the internal coordinates of a trajectory and to analyze the final states after the collision. Another example of the use at low order perturbation theory is given in (94).

Gutzwiller has developed a significantly different technique (95–99) for the semiclassical calculation of bound state properties. His method begins with a Green's function approach used to calculate the semiclassical propagator. Quantization conditions are then derived which depend upon the location of a family of periodic orbits. The method is intended to be appli-

cable to both nondegenerate and degenerate systems as well as to the chaotic regime. Gutzwiller's method has not been extensively tested, perhaps partly because of the difficulty involved in obtaining a family of periodic orbits. In an early application of this method by Miller, only one periodic trajectory was used per state (100) but was found to give spurious results (72). Miller later developed corrections for this method (101), by replacing a Gutzwiller expansion by a sum in the vicinity of a periodic orbit to yield an approximation to the tori found by Marcus and coworkers. Families of periodic orbits have been used to calculate eigenvalues and/or densities of states (98, 102).

Berry & Tabor (103a,b) have obtained in a different way Gutzwiller's formula for the density of states in terms of families of periodic orbits. There was excellent agreement between their semiclassically calculated density of states, and the quantum result for a model problem. The calculations showed significantly more structure than the classical density of states.

Gerber & Ratner (104) have used semiclassical wavefunctions within a self-consistent field quantum calculation for two coupled oscillators, with good results for the eigenvalues.

Gutzwiller has applied his method of using families of periodic orbits to a system stated to be chaotic, the anisotropic Kepler problem, with quite reasonable results (99). This problem is a nearly degenerate system, and for a truly degenerate system a single periodic orbit would suffice. It would be interesting to see if this method can be used to locate semiclassically the eigenvalues for anharmonically coupled oscillators in the classically chaotic regime. Once again, one should make sure that spurious eigenvalues do not, as in the one-periodic-trajectory case (72), also appear.

In the chaotic regime only two of the above techniques have located the eigenvalues. Swimm & Delos (87a–c) reported 60% of the chaotic eigenvalues in the Hénon-Heiles system (a 1:1 resonance system) with good results in some cases. Jaffé & Reinhardt (79) reported values for all of the eigenvalues of this system. More detailed calculations on other chaotic systems are needed to reach a conclusion on the applicability of these techniques. It should be pointed out that the above system may, for the value of the perturbation parameter chosen, not be quantum mechanically chaotic, as discussed in the next section. The above perturbative techniques are expected to break down in the quantum mechanically chaotic regime, i.e. in the regime of overlapping accidental Fermi resonances considered below.

An approach that is applicable to both the quasiperiodic and the chaotic regime is the quantization of the energetically accessible phase space

volume. However, this method can only be expected to locate the levels to within half the level spacing (38a,b, 105). Of course, any method proposed for the chaotic regime must do better than this to represent a quantitative improvement.

QUANTUM MECHANICS

The dramatic distinction between the classical dynamics in the quasiperiodic and chaotic regimes has led to the question of whether this behavior reflects qualitatively different motion in molecular quantum mechanics, and, if so, how. In the previous section we discuss how semiclassical techniques are being used to bridge the gap between classical dynamics and the quantum mechanics of coupled vibrations in molecular systems. The correspondence has been successfully demonstrated in the quasiperiodic regime. In the chaotic regime the correspondence is not as satisfactory, since an adequate, generally applicable method of describing the semiclassical mechanics in the chaotic regime has not been developed. Reflecting this situation, numerical experiments on the Schroedinger equation are now being used to search for a quantum analogue of classical chaos, just as numerical experiments with Hamiltonian mechanics were originally used to gain insight into classical chaos.

Studies of quantum chaos have only very recently begun to be reported, and as a result the conceptual understanding of the phenomenon is not as complete as in the quantum quasiperiodic case. In several examples of these numerical experiments the time-independent properties of the wavefunctions in coordinate space and their eigenvalues have been investigated. The Schroedinger equation was solved by a variational calculation, by expanding the wavefunction in harmonic oscillator or other wavefunctions, and the resulting variational matrix was diagonalized to obtain eigenvalues. The convergence of this solution depends upon the completeness of the original expansion of the wavefunction.

One definition for an ergodic (chaotic) quantum state, proposed by Nordholm & Rice, is that its wavefunction have contributions from a large number of basis functions (106a–c). Each of the "quantum ergodic" wavefunctions, so defined, was termed global and the remaining ones, local. A number of two and three dimensional systems of coupled oscillators were studied and in general at higher energies, where the motion is usually classically chaotic, they found more global states. Conversely, at lower energies, where the classical dynamics is generally quasiperiodic, the wavefunctions were assigned as being predominantly local. However, it was recognized that the characterization of "globality" vs "locality" was basis set dependent (106b).

Subsequent work by Noid & Marcus (73) showed, instead, that although the global states were the ones that mixed the energies of the zeroth order Cartesian coordinate modes, they did so in a nonchaotic way: all of the states labeled global were found to correspond semiclassically to quasiperiodic states, while many of the states labeled local corresponded instead to classically chaotic states. The states which have extensive "mixing" (i.e. global) were those with moderately large and large internal angular momentum l (hence the latter is not ergodically disturbed in these global states) and had trajectories analogous to the one in Figure 2. These higher l states are precisely the ones for which the tori persist, in this Hénon-Heiles system, when the energy is increased in the increasingly classically chaotic regime. In summary, these results showed that one cannot equate modal energy mixing with the opposite of quasiperiodicity and hence with classical chaos. To do so leads semiclassically to inconsistencies. Characterization of globality vs locality is nevertheless very useful, since it is desirable to know for experiments when modal energy mixing occurs, regardless of whether it does so in a "quasiperiodic" or "chaotic" way. Classical examples of quasiperiodic modal-mixing states are given in Figures 2 and 3, and of a quasiperiodic "modal nonmixing" state in Figure 1.

Wavefunctions are difficult to calculate accurately, as compared with eigenvalues, unless the basis set is large enough and particularly appropriate. We return to this point later in the calculation of Wigner functions. For example, Noid & Marcus noted that the Hénon-Heiles system has C_{3v} symmetry (73) and that certain pairs of states must therefore have identical dynamical properties. With a given basis set about 50% of these equivalent states appeared (106a,b) to have different global-local properties.

Heller has commented further on this system (107), noting that since the system had C_{3v} symmetry it must have two symmetry classes of wavefunctions which will not mix. Therefore, in an isolated system a wavepacket of one symmetry type cannot chaotically mix with one of another symmetry type, and it cannot be truly "ergodic." There has been some discussion in the literature on whether a measurement would break this symmetry and thus make the mixing actually observable (108).

Stratt et al (109) have extended the Nordholm & Rice criterion. They introduced a type of "natural orbitals" for the system (the smallest basis set in which the exact states can be adequately described). The local-global suggestion was then examined using the nodal patterns and natural orbitals. This method gave good agreement with the classical mechanics. Although this method is no longer as basis set dependent, the method does depend on the coordinates used in selecting the "best" small basis set. The semiclassical results (73) obtained earlier suggest that for the Hénon-

Heiles system polar coordinates are more appropriate than Cartesian ones, and it would be interesting to use them. Evidence that classical chaos doesn't necessarily imply quantum chaos has been obtained by Kay (110) and by Noid et al (38a).

Another example of interest is the Fermi resonance system where, for a particular value of the perturbation parameter, one can separate the variables (56). Such a system is quasiperiodic. If one describes the wavefunctions in terms of an (x,y) basis set, one would presumably conclude that many of them are global (reflecting, however, a nonchaotic modal energy mixing). This provides again an example where global does not imply quantum ergodicity or quantum chaos (the spectrum is quite regular), a distinction frequently overlooked; globality is related to the useful concept of modal energy mixing. It might be useful to label such states (and the non-low angular momentum ones in the Hénon-Heiles system) specifically as "modal energy mixing states."

Percival (111a) conjectured, by analogy with the classical behavior, that the spectrum would be "irregular" for a quantum mechanically ergodic system and "regular" otherwise. He also postulated that another criterion for the quantum analogue of classical chaos would be a large sensitivity of the eigenvalue to a perturbation, reflected in the second derivative of the eigenvalue with respect to a perturbation parameter, in the chaotic regime. Pomphrey (111b) then used variational calculations on a model system (Hénon-Heiles) for three values of the perturbation parameter and calculated second differences of each of the eigenvalues. In the calculation there were no large values of the second difference in the classically quasiperiodic regime, whereas there were several large values in the chaotic regime. Noid et al (38a,b) found in a later calculation on a different system (Hénon-Heiles with a different value of the perturbation parameter) that the second differences varied smoothly with energy in each sequence of states. Except for two eigenvalues (the states which involved an avoided crossing, discussed below), there were no large second differences.

In a different problem, the libration-rotation of a pendulum, one may anticipate a relatively large second difference for the state just below the rotational barrier when the perturbation parameter is changed to lower the barrier. For this case the second difference detects a qualitative change in the classical dynamics (though not actually chaos, since this is a one-dimensional system).

The behavior of the probability density $|\psi|^2$ in coordinate space was examined for a system with a 1:2 Fermi resonance (56) in the zeroth order Hamiltonian. For this system the semiclassical "eigentrajectories" (trajectories which satisfy Eq. 4) occupied a limited amount of the ener-

getically accessible coordinate space. The trajectories spread out over the entire coordinate space in the chaotic regime. When plots of $|\psi|^2$ were compared to eigentrajectories in the quasiperiodic regime and to chaotic trajectories at higher energies, it was found that in both regimes the largest probability was in the same region of coordinate space as the trajectories (56), as in Figure 8.

McDonald & Kaufman (112) and Stratt et al (109) have used an approach analogous to that of examining $|\psi|^2$ above, namely they examined the location of the nodal lines of the wavefunction in coordinate space. For several examples it was shown that in the quasiperiodic regime the nodal lines could be easily assigned quantum numbers but they became very complicated and irregular in the chaotic regime. For some states, at least, the overall pattern may correspond to that expected for an avoided crossing of eigenvalues, described below. A regular nodal pattern was also seen in [(37) Figure 7].

Berry & Tabor (113) and Zaslavskii (114) have postulated that a statistical distribution of eigenvalues defined by Wigner (115, 116) would occur in a quantum ergodic system. McDonald & Kaufman (112) tested this postulate for the stadion (cf 117) (which has been analytically proven to be classically ergodic) (118). They found that the distribution of eigenvalues was statistical and that in a separable system and hence quasiperiodic one, the distribution was significantly different, as predicted (113).

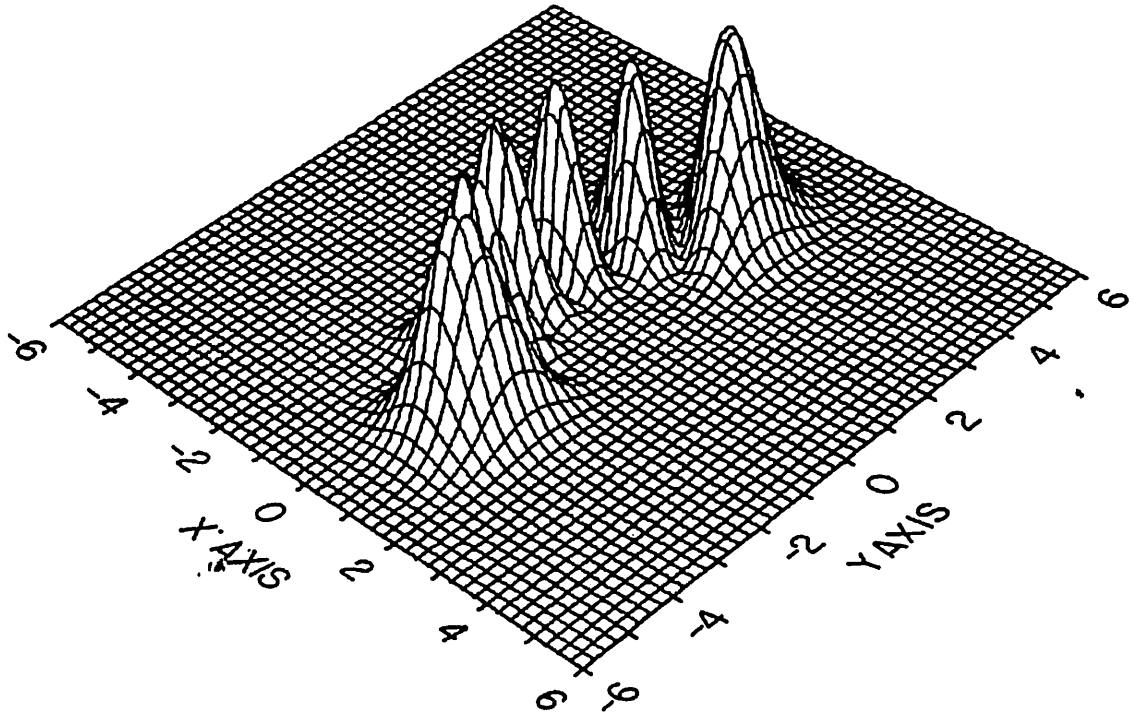

Figure 8 Plot of the square of the wavefunction, $|\psi|^2$, for the system described by Figure 3. Figure 3 is the trajectory which corresponds semiclassically to this particular wavefunction.

It has been suggested (106a, 119, 120) that the Wigner functions would more directly reflect the underlying classical dynamics. Hutchinson & Wyatt (121) calculated the Wigner functions for the Hénon-Heiles system and found a qualitatively different distribution at low and high energies, a result that seemed to agree with the corresponding classical behavior in the surfaces of sections. However, it is clear from one of Hutchinson & Wyatt's figures (Figure 2b) that in the intermediate energy regime the basis set was too small to resolve $+l$ and $-l$ states. Even less resolution would be expected in the higher energy "chaotic regime." Accordingly, it would be useful to pursue these interesting calculations with the aid of a larger basis set so as to distinguish neighboring states.

The time evolution of wavepackets composed of a sum of eigenstates has been investigated by several groups. Brumer & Shapiro (122) used a wavepacket with a Gaussian spread over energy states, and saw no major distinction between the behavior of an ergodic and a separable system. Kosloff & Rice (123) interpreted this in terms of a newly defined quantal Kolmogorov entropy which predicted no change. However, since their (123) quantity is always zero, it wouldn't detect any change, even as $\hbar \to 0$. Heller (124) has emphasized that implicit in the choice of Brumer & Shapiro's wavepacket was a stochastic nature (i.e. microcanonical-like) and no difference in the two regimes would be expected. He then presented an example of wavepackets highly localized in coordinate space whose time evolution does change considerably in the two regimes. Weissman & Jortner (125) looked at two Gaussian wavepackets of Hénon-Heiles states, one concentrated in the classically quasiperiodic region and the other in the classically chaotic region of phase space, both at the same energy. They found rapid dephasing of the initial coherence in the later case. Koszykowski et al (41) have seen a behavior similar to that described by Brumer & Shapiro and by Heller, but for the time-correlation functions of classical dynamical quantities: the canonically averaged correlation functions showed only smooth changes between the regimes while modal ones changed somewhat more dramatically (41). Criteria for stochastic and nonstochastic behavior, using wavepackets, have been discussed by Heller (126).

Noid et al (38a,b) examined the quantum mechanical spectrum for the Hénon-Heiles system, and observed, for the perturbation parameter used, a continuation of the sequences of eigenvalues, i.e. a regular spectrum, into the classically chaotic regime. That is, using the spectrum as a criterion, classical chaos did not necessarily imply quantum chaos.

They then studied the behavior of the eigenvalues of the Hénon-Heiles system as a function of the perturbation parameter. When these eigenvalues were plotted as a function of the perturbation parameter, it was

discovered that the only pair of eigenvalues having a large second difference near the value of the Hamiltonian parameter used in (106a–c) and in (73) underwent an avoided crossing there (terminology borrowed from that for electronic states where crossings and avoided crossings occur as a function of nuclear coordinates). These two states were among those, it is interesting to note, for which Delos & Swimm (87a–c) did not report good eigenvalues. The avoided crossing behavior of the eigenvalues was then examined on a model of a triatomic molecule (127), which had many more states than the previous system. This calculation demonstrated no avoided crossings in the classically quasiperiodic regime, but displayed many overlapping avoided crossings in the chaotic regime.

A summary of our view of the significance of these crossings is the following: The introduction of a perturbation λ into a quantum mechanically integrable system can distort the shapes of the original wavefunctions gradually with increasing λ. Then, near some λ, a pair of states may undergo an avoided crossing (an accidental Fermi resonant interaction) (38a,b) and one achieves near this λ a drastic change of the shape of each of the two wavefunctions (which is now a linear combination of the previous two wavefunctions) with a subsequent small change of λ. If a state participates simultaneously in many such resonances, its shape begins to take on a statistical character, and it can be termed "chaotic" (128, 129). This ability to participate depends on the density of quantum states, and so on the size of $\hbar$.

The onset of extensive avoided crossings clearly produces irregular spacings of eigenvalues instead of regular ones, i.e. produces an irregular spectrum instead of a regular one. This feature of avoided crossings thus provides a mechanism, a purely quantum mechanical one, for the irregular spectrum conjectured (111a) by Percival.

Avoiding crossings have also been examined for stadion-like problems (105, 130). They were also examined by Ramaswamy & Marcus (131), who applied quantum perturbation theory to the Hénon-Heiles Hamiltonian to study the behavior of the eigenvalues. They found many more crossings for Pomphrey's system (111a,b) than for Noid's (73), and, correspondingly, there were many more large second differences in the former. The simple perturbative approach does not distinguish between crossings and avoided crossings, but one can do so by the use of degenerate perturbation theory at the crossing (131). States of unlike symmetry can cross, and in an actual crossing there is no "state mixing." For example, a particle in a two dimensional box exhibits many crossings of the energy levels when the ratio of the length of the two box sides is changed. The significance of multiple avoided crossings has not yet been fully established, but we believe that it is the quantum counterpart of classical

overlapping resonances (129). Some interesting results on chaos and quantum maps are discussed in (64, 132–134).

It is well known that a correspondence between classical and quantum mechanics is obtained by replacing classical Poisson brackets $\{\ ,\ \}$ by commutators $[\ ,\ ]$ and dynamical variables by Hermitian operators (135). It has been suggested (136), correspondingly, that some insight into the quantum analog of classical integrability is obtained by using this operation and the following property of classical integrability. A classical dynamical system of m coordinates is defined as integrable (i.e. having m constants of the motion) if there exist m functions F_i in phase space for which $\{F_i, F_j\} = 0$ (137a, cf 137b), with $F_1 = \mathrm{H}$.[4] Correspondingly, for an analogous m-dimensional system in quantum mechanics we (136) might define as a quantum mechanical integrable system one for which there are m operators $\mathbf{F}_i$, with $[\mathbf{F}_i, \mathbf{F}_j] = 0$—i.e. one for which a complete set of commuting observables actually exists. Examples are systems that permit separation of variables. Another and different example is the quantum mechanical Toda lattice (138). From these m commuting operators there are m constants of the motion, and they yield a set of m quantum numbers. Because of the existence of such constants, the eigenvalues can be characterized by sets of m integers, and in turn, this characterization gives rise to regular series of spectral lines (without invoking a semiclassical argument). Because of the existence of these sets of integers and their implications in terms of nodal surfaces, one expects to find, correspondingly, "regular" wavefunctions, with regular nodal patterns in the different spatial directions—directions which are better described in some coordinate systems than in others. Similar conclusions were reached earlier from pictures of wavefunctions by Noid et al (139). This picture is supported by the corresponding semiclassical eigentrajectories, each of which is confined to the same spatial region in which the corresponding regular eigenfunctions are concentrated (56).

In Hamiltonian systems which are "close" to these integrable systems, it was suggested (136) that qualitatively similar quantum mechanical behavior might occur for most states in the nearly integrable domain, i.e. regular, if not sharp, nodal patterns, and regular series of spectral lines. An avoided crossing of two such states results in states whose wavefunction becomes approximately a linear combination of the two previous wavefunctions, and the nodal pattern becomes a composite of the two previous nodal patterns. Further, the splitting near the avoided crossing

[4]That is, these F_i are integrals (constants) of the motion, e.g. the good action variables.

introduces a local irregularity in the spectrum. When a state becomes simultaneously involved in many overlapping avoided crossings at the given value of the perturbation parameter, the wavefunction becomes extended in all directions and tends to "occupy" much of the classically energetically accessible region (128, 139).

We have noted, because of our results in (38a,b), that classical chaos may be a necessary but not a sufficient condition for quantum chaos. Additional conditions for quantum chaos have been suggested (129, 140). These conditions cannot be satisfied when the spacing of adjacent states is too large. In some systems, judging from the numerical results, these conditions appear to be satisfied, since quantum and classical chaos (the former described via many overlapping avoided crossings) appear to begin in the same energy region (127, 131). Kay has extended (140), with results similar to those in (129), and has tested the theory (110).

The classification described earlier for quasiperiodic versus chaotic states is designed for bound states. Bound states are appropriate for the description of the absorption steps in IR multiphoton absorption energies below the dissociation energy, in fluorescence and absorption spectra, and in internal conversion and intersystem crossing, where the electronic coupling is also considered. States with energy above the dissociation limit enter into treatments of unimolecular reactions, chemical activation, and IR multiphoton absorption in the true continuum. Bound classical quasiperiodic states can exist indefinitely at energies above the dissociation limit (75). Semiclassically, their quantum mechanical counterparts are "quasiperiodic" quantum states (75) that are, however, connected to the outside by leakage of the wavefunction beyond the caustics and thereby are unbounded.

Yet to be classified are the unbounded states, both classical and quantum. They involve families of trajectories leading from the separated particles to the formation of the vibrationally excited parent molecule and then to a redissociation. These states might, if the system spent a long enough time in the parent molecule's phase space, appear as largely quasiperiodic or as largely chaotic before reemerging. The trajectory's spectrum for the time spent by the trajectory in the molecule, if that time is long enough, or perhaps the rate of separation of neighboring trajectories, could again be used to distinguish chaotic from "quasiperiodic-like" cases. In the quantum case an individual unbound state corresponds to a resonance and perhaps, by analogy with the bound states, it could be classified as "quasiperiodic" or "chaotic." This is an area where further study is needed. For simplicity, we use this classification for unbound states, with

spectral properties analogous to those for bound quantum states. In either case the state has a decay width (as do also the bound states, when coupling to the radiation field is included).

CORRELATION FUNCTIONS AND SPECTRA

In the sections above we are principally concerned with the phenomenology of classical and quantum dynamics of coupled anharmonic molecular vibrations, both at low and high energies. A particularly interesting feature, one directly connected with some experimental observations, involves the spectroscopic properties of the system. Such power spectra are also of interest in other fields such as turbulence in fluids (34) and in confined plasmas (33), although we make no attempt to review these nonchemical areas. Using the new high resolution state selected spectroscopic methods, applied to low pressure and low temperature systems, as in some molecular beams for example, a detailed examination of the spectra in the two regimes would be of much interest.

Noid et al (36–38a,b) developed a semiclassical method of obtaining vibrational power spectra from classical trajectories. They used the zeroth order eigentorus (the torus satisfying Eq. 4) to calculate the autocorrelation function of any dynamical variable. Then, as prescribed in linear response theory, the corresponding absorption (power) spectrum is given by the Fourier transform of the correlation function. An appropriate correspondence principle interpolation was then used to obtain the transition frequencies in the quasiperiodic regime. The agreement between this calculation and an exact quantum calculation was excellent for two and three dimensional model systems. Later deficiencies in intensities of ordinary FFT numerical methods were corrected and, using the same method, intensities of lines were predicted using a correspondence principle (38a,b, 141). They were in excellent agreement with a "converged" quantum calculation obtained using variational wavefunctions. Recently, fundamental and overtone frequencies and intensities were calculated, from the classical spectrum of a Morse oscillator (141), using the correspondence principle. Again, good agreement (now analytic) was found with the quantum mechanics. Noid et al (36–38a,b) have also found that when the classical motion becomes chaotic the spectrum becomes much broader and consists of many more lines. (Ultimately for an infinite time trajectory these lines may yield a continuous band.) Powell & Percival (40) have extended this classical-trajectory-spectral method by defining a Fourier entropy which is a measure of the number of significant Fourier coefficients. The Fourier entropy was found to change dramatically in the

chaotic regime and was proposed as a test for chaotic motion. Hansel (39) has also used the classical-trajectory-spectral method and numerically found that the width obtained was proportional to the k-entropy of the trajectory, a measure of the extent of mixing. A corresponding quantity has been evaluated in fluid mechanics. The velocity power spectrum of a laminar flow is sharply peaked and consists of a few lines, while for turbulent flow it becomes very broad and consists of many more frequencies (34).

Heller et al (124, 142a,b) have developed a method for calculating the vibrational part of vibronic spectral lines obtained when a wavepacket is excited in a Franck-Condon transition. In the quantum calculation one considers the correlation function for the evolution of a wavepacket that was originally localized in coordinate space. The Fourier transform of this time correlation function then yields the quantal results. In this semiclassical calculation they use a small ensemble (e.g. < 10) of trajectories initially located in some region of coordinate space relevant to a Gaussian distribution. Short-time trajectories are then used to calculate the correlation function, and via a Fourier transform the spectrum is obtained. Several examples were given and the frequencies and intensities of the quantum and classical calculations agreed well. This short-time trajectory method has been used for obtaining the envelope of the vibrational spectrum arising from the lowest vibrational state in an electronic Franck-Condon transition. Longer trajectory times begin to show more of the vibrational structure. The results may be sensitive to the particular trajectories chosen for the ensemble. A Gaussian distribution is most appropriate for a vibronic excitation from the zero-point vibrational level of the initial electronic state. If one wished, instead, to describe the pure vibrational spectrum of some particular ensemble of initial quantum states (or of one of them) one should presumably choose a corresponding ensemble of eigentrajectories (or one of them), rather than a Gaussian ensemble, and use the method of (36–38a,b).

Mo developed a perturbative approach to examine the behavior of the autocorrelation function of the distance of the phase space point from the origin (57). She postulated that the correlation function would behave exponentially in the chaotic regime, and calculated the critical energy for chaotic motion with excellent results. Koszykowski et al (41) investigated various correlation functions of dynamical variables averaged over a microcanonical ensemble. They found, in general, a smooth evolution of each time microcanonical correlation function as the energy was increased from the quasiperiodic regime into the chaotic regime, with no abrupt change on entering the chaotic regime. This result seems to be in qualita-

tive agreement with Heller's argument (126) that a nearly microcanonical wavepacket (a packet over a Gaussian distribution of energy levels) is not sensitive to the transition between regimes.

When the same classical autocorrelation functions were calculated and only phase averaged, not microcanonically averaged, a more obvious change from oscillatory to decaying behavior (with some superimposed oscillations) was observed (41). The decay time for the mode energy autocorrelation gives information about the time scale for intramolecular modal energy relaxation. This modal energy relaxation has important experimental implications, as discussed below. Abarbanel (143) has demonstrated that in the chaotic regime the behavior of phase averaged time correlation functions will be in general oscillatory and decaying.

There has been much interest lately in highly excited overtone spectra (13, 144a–d) and in the concept of local modes vs normal modes. For some systems it has been found that local modes (bond stretches) can more usefully be used to assign the spectra than normal modes. In a normal mode treatment the wavefunction ψ of an excited normal mode is concentrated along that normal mode axis in a configuration space in which the axes are the normal mode coordinates. In a local mode treatment, a local mode excited ψ would be concentrated instead along a bond displacement direction in that space. (This direction is at some angle to each normal mode direction.) There is some evidence from a two-coordinate study by Lawton & Child (145a,b) that in H_2O the trajectories are concentrated along such directions in, at least, some highly excited vibrational states. Because of symmetry, one has symmetry-adapted local modes (146a), whose wavefunction is composed approximately of a linear combination of the individual local modes (chemical bonds). In actual molecular systems, because these (symmetry-adapted) local modes are also coupled to many other vibrations, there is a broadness of the spectral lines, which is an indication of intramolecular relaxation. It is not yet known whether this relaxation is of the energy loss kind or of the pure dephasing kind.

An interesting study of unimolecular decay rates in the tunneling region of the Hénon-Heiles system was made by Waite & Miller (146b). Apart from a symmetry-induced specificity they found that the decay rates were well represented by RRKM theory plus tunneling. Perhaps this result was due to the many (3) exit channels, as they noted. Many of the states were modal mixing. Results obtained instead with a single exit channel potential surface, and also with presumably little or no modal-energy mixing, showed non-RRKM behavior.

CLASSICAL TRAJECTORIES

Many classical trajectory calculations have been performed related to the experimental problems discussed above. Because of limitations of space we merely list a sample of these here. Reviews of the trajectory studies for unimolecular reactions have been given by Bunker (147a,b) and Hase (2b).

The lifetimes of vibrationally excited dissociating species have been studied using trajectories by Bunker et al (50, 147a,b, 148), Wilson et al (149a,b), Wolfe & Hase (150a,b), and Brumer & Karplus (151). These studies use relatively short times because of computer time. Particularly by Bunker and by Hase, the lifetimes were compared with RRKM-type lifetimes. The time-dependent energy redistribution in a molecule was investigated by Parr et al (152). Energy distribution of the reaction products of a dissociated molecule were examined by McDonald & Marcus (153) and by Wolf & Hase (150a,b), who looked at exit channel effects. The lifetime of a van der Waals complex was studied by Woodruff & Thompson (154). Resonances in quasibound states have been located semiclassically by use of trajectories and compared with quantum calculations, by Noid & Koszykowski (75). Kay (110) used an ensemble of trajectories originating from some volume element in a zeroth order quantum number (zero-order action variable) space and studied their rate of appearance in other volume elements of that space. Comparisons were made with a corresponding quantum mechanical calculation.

There have been a number of trajectory studies of infrared multiphoton dissociation. Noid et al (155a–c) studied the energy distribution of the reaction products of infrared multiphoton dissociation and, along with Hansel (156a,b) and Ramaswamy et al (157), investigated the time-dependent energy absorption in this process. SF_6 in a laser field was simulated by Poppe (158). The behavior of a diatomic molecule in a two-laser field was investigated by Noid & Stine (159a,b), who also looked at the effect of laser polarization (160a,b).

Energy transfer in a collision of an atom with a collinear triatomic molecule has been studied in the chaotic and quasiperiodic regimes by Shatz & Mulloney (161) and by Noid & Koszykowski (162a,b). Relatively chaotic and nonchaotic trajectories in bimolecular reactions have been studied by Duff & Brumer (163) and by Wyatt and co-workers (164a–c). Using a microcanonical ensemble rather than trajectories, Liu & Noid (165) have estimated Franck-Condon factors in the chaotic regime.

RELATION TO EXPERIMENTAL RESULTS

In relating experimental data to studies described in the preceding sections a number of questions arise: When do the data indicate the occurrence of intramolecular energy randomization and how rapid is it? How is such randomization or lack of it related to the theoretical studies of quasiperiodic quantum states (i.e. those with a regular though possibly exceedingly complex series of spectral lines) and chaotic quantum states, for a system containing many coordinates? The quasiperiodic states may be of two kinds, those which mix and those which do not mix the energies of the unperturbed modes. Those which mix are termed "modal energy mixing." In a modal coordinate space (e.g. bond modes or normal modes), a nonmodal mixing state may nevertheless have its principal axes (those of the corresponding box-like trajectory) inclined at an angle to that of some coordinate excited in an experiment (128). In that case the excitation of even this state excites two modes.

One mechanism for intramolecular randomization directly involves the preparation of the state, which can be a wavepacket of many "exact" vibrational states. The subsequent dephasing due to energy differences among the states corresponds to a randomization, a mixing of the energy among the zeroth order modes, regardless of whether the individual eigenstates are quasiperiodic or chaotic. In this case there is a relaxation time associated with forming this more randomized state. Of course, if each quantum state is already chaotic its behavior is instantaneously "microcanonical." The rate of the randomization in a wavepacket will depend on the detailed nature of the states and on the packet originally prepared: at low energies, where the individual states are not chaotic and where the density of states is small, there may be little, if any "randomization." There may be differences, too, in the behavior of a dissociating system and a nondissociating system which typically will have a "stiffer" potential energy function and which frequently has lower vibrational energy. We consider next some of the specific data.

One of the most common sources of information in the past on intramolecular energy transfer has been unimolecular reaction rates (1a,b). Collisional activation leads to the formation of vibrationally-excited molecules, which either subsequently decompose unimolecularly or are collisionally deactivated. In the RRKM theory, it is assumed that each reactive vibrationally excited species explores all the zeroth order, microcanonically accessible quantum states available to it before decomposition, consistent with the given total energy and angular momentum

(perhaps with some adiabatic rotations).[5] Thereby, in one view, largely "chaotic" or largely modal mixing quasiperiodic quantum states are tacitly assumed—each such state senses most parts of the accessible "phase space." Another mechanism for randomization (128) is discussed below. Typically, RRKM theory has been successfully used to interpret a large body of data on unimolecular reactions and on chemical activation (1a,b, 2a,b, 17).

In the alternative theory of Slater (15), one assumed that all vibrations are harmonic; the "phase space" explored by the molecule was limited by the m constants of the motion (for m vibrations), the m maximum vibrational amplitudes (or the m vibrational action variables). One severe resulting constraint, for symmetric systems such as cyclopropane, was that because of the symmetry assumption throughout the dissociation of a molecule, only about half of the vibrations could participate. Actually, during the dissociation the symmetry is broken, and so the assumption that symmetry is maintained, which followed directly from the harmonic oscillator assumption, leads to a large error. The effects of the introduction of substituents to destroy the initial symmetry (170, 171a,b), which would be small in the RRKM-type theory but large in Slater's theory, were indeed experimentally found to be small (reviewed in (17)). Anharmonic studies for 1:1 degenerate systems (73) showed that even a little anharmonicity permits extensive energy sharing between the unperturbed degenerate modes.

In a formal modification (24) of the Slater approach, which removes the above restriction, quasiperiodicity is assumed, but not harmonicity, and so the correct tori, assumed to exist, are used. The dissociation rate constant of a vibrationally excited species now depends on all the action variables $\mathbf{J}$ instead of only the energy and angular momentum L, and is written as $k(\mathbf{J})$. In the quantum case one specifies instead the values of the set of quantum numbers $n_1, \ldots, n_N$, and so one can write $k(\mathbf{n})$, if the states $\mathbf{n}$ were individually excited in a collision. When $k(\mathbf{n})$ for a given E and L does not fluctuate too widely with $\mathbf{n}$, the expression simplifies to

[5]Other forms of RRKM-type, i.e. statistical, theory are (*a*) phase space theory (166a,b), which assumes that the reaction has a loose transition state (no steric factor for the reverse reaction, a bimolecular association); (*b*) statistical-adiabatic theory (167), which assumes vibrational adiabaticity (e.g. 168) along the exit channel to define the transition-state separation distance for each outgoing internal quantum state; and (*c*) statistical-dynamical theory (169a,b), which includes in a vibrational adiabatic statistical way exit channel effects. In the case of a loose transition state (*b*) and (*c*) reduce to (*a*).

yield the RRKM expression. Thus, information about the dependence of $k(\mathbf{n})$ or $\mathbf{n}$ in a given energy interval is of particular interest.

The collision of a molecule with a large second molecule will probably initially excite some portion of the second molecule, the nearest part, for example. Quantum mechanically, we have suggested that a wavepacket of the exact vibrational quantum states is excited by the collision (128), and that the ensuing motion of this wavepacket provides an intramolecular energy redistribution. If a wavepacket is evenly distributed over a microcanonical set of states (41) or over a broad set of states of different energies (128, 142a,b), its behavior may or may not depend on whether those states are "chaotic" or "quasiperiodic." In any case, the quasiperiodic treatment in (24) would be modified. One would use, as a first approximation, some wavepacket-averaged $k(\mathbf{n})$.

Some information, largely indirect, is available experimentally on the behavior of the vibrational states. For example, excitation in different CH vibrations for a vibrationally excited species has been produced by Reddy & Berry using various laser spectral lines (12a,b). If the collision-free decomposition rate constant is a monotonic function of the energy, then either the excitation has produced a set of chaotic quantum states, or the rate constant does not vary particularly among the quasiperiodic unbound states, for any given energy, i.e. $k(\mathbf{n})$ can be replaced by a microcanonical average. In either case, RRKM-type theory becomes applicable. Experimental studies with methyl isocyanide revealed very little, if any, deviation from monotonic behavior (12a,b), while studies with allyl isocyanide revealed some fluctuations of perhaps 50%, or less in some cases, from the monotonic curve (12a,b). It was already noted above that small enough fluctuations in $k(\mathbf{n})$ with $\mathbf{n}$ at a given E and L would yield behavior indistinguishable from RRKM. Fluctuations of 50% might well not cause significant deviations from RRKM-type unimolecular reaction rate vs pressure plots. The most remarkable and important finding in these results, sometimes overlooked, is that state-selectively prepared molecules (12a–c) have dissociation rates relatively close to (factor of 5 or better) those predicted from related unimolecular reaction studies, e.g. predicted from RRKM at the same energy. It would be very desirable to have experimental thermal unimolecular reaction rates for all three molecules studied in (12a–c), for a more accurate comparison.

Another source of exciting different sets of vibrations is via electronic excitation, e.g. from S_0 to S_1 states of aromatic-like molecules, and from S_0 to S_2 followed by internal conversion to S_1. The detailed interpretation will ultimately involve analysis of the fates of the various excited states, including measurements of the triplet states formation rates ($S_1 \rightarrow T_1$ at

low energies, $S_1 \rightarrow S_0$ at high energies). However, a "bump" in the plot of fluorescent lifetime ($\sim$ 20%) (172) and a "step" in the nonradiative decay rate vs excitation near the S_2 excitation threshold (173) have been attributed to a difference in vibrational distribution of S_1 species produced by the two routes (172, 173).

Chemical activation produces an initial excitation very different from the excitation produced in unimolecular reactions, and yet the two sets of results yield consistent agreement for the lifetimes of the vibrationally excited species (2a,b). The simplest interpretation, and the one normally given, is that RRKM-type theory applies in each case, i.e. there is energy randomization of the vibrationally excited species in both cases. One question that arises is whether or not the state prepared by chemical activation involves a superposition of an almost microcanonical distribution of quasiperiodic states (cf 174).

Translational (3,4) and vibrational (11, 175) energy distributions of products of chemical activation have been studied in molecular beams. The results can largely be summarized as follows: When the transition state in the exit channel is "loose" and the lifetime of the intermediate molecule is not too short, the translational energy distribution obeys RRKM-type theory (3, 11, 175, 176a,b). When the lifetime of the intermediate is too short, as in

$$Cl + CH_2CHCH_2Br \rightarrow Br + CH_2CHCH_2Cl,$$

(estimated to be < 1 ps (176a,b)) there is deviation from this theory (176). When the transition state in the exit channel is "tight," exit channel effects can occur (169a,b, 177), and then even when the distribution in the transition state is RRKM-like the final distribution need not be (169a,b, 177).

The mechanism of an intramolecular "randomization" in a molecule (radical) formed by chemical activation, or vibrationally excited by collision or by infrared absorption, may involve any of the following:

1. A wavepacket of vibrational states is formed containing appreciable contributions from most of the "exact" vibrational eigenstates of the molecule at that energy. It dephases and the molecule then displays a statistical microcanonical behavior, though not necessarily a single exponential decay rate.
2. All the vibrational states of the molecule may be largely chaotic (or modal mixing quasiperiodic) and so have somewhat similar properties.
3. The states are largely not modal-mixing quasiperiodic, though some "randomization" from the prepared state occurs as a result of dephasing.

To distinguish No. 2 from No. 3, one can, in principle, after allowing sufficient time for dephasing to occur, follow the time-decay of the energetic molecules. They will decay via a single exponential in No. 2, if the energy distribution is narrow enough, but in a more complicated way in No. 3.

It is interesting to note the behavior of the product C_2H_3F of the chemical activation step (11),

$$F + C_2H_4 \rightarrow C_2H_3F + H.$$

Here, the intramolecular collision-free randomization, judged from its infrared chemiluminescence, is apparently not complete, even though the C_2H_3F has survived for milliseconds (178). The presumed deviation of the intramolecular energy distribution from the microcanonical one was not large, a factor of two or less deviation in some modes. Its persistent nonequilibrium distribution may be due to the low density of states (176a,b, 178), sparsity of internal resonances, and/or a presumed stiffness of the potential energy function at the low vibrational energies involved.

In infrared multiphoton absorption it seems reasonable to attribute the coherent behavior of the absorption in the lower energy states to quasiperiodic states (155–157). It has been concluded in a recent study by Stephenson et al (179) of the energy distribution of products in the multiphoton dissociation of CF_2CFCl that the behavior is RRKM-like. Similar conclusions had been drawn by Lee and collaborators (6) in their many studies of the translational energy distribution of the products. The uniqueness of the latter interpretation was questioned by Thiele et al (180). Subsequently, measurements of the lifetime of the parent molecule, SF_6, were inferred from the secondary dissociation of the SF_5 to support the original view (181). The original articles (6, 180, 181) contain a more detailed discussion. In an interesting study by Richardson & Setser (182), the CF bond in CH_2FCH_2Br was excited with a laser and the HBr:HF ratio was measured and found to agree with statistical theory. These experiments and those on other systems are discussed in an excellent review by Oref & Rabinovitch (17a).

Infrared multiphoton absorption has a number of other aspects particularly related to intramolecular randomization: relation of the photodissociation IR spectrum (plot of amount of absorption vs wavenumber at a given intensity) to the low signal IR absorption spectrum, and the behavior of the absorption cross-section as a function of fluence. The prevalent picture of IR multiphoton absorption is that successive photons are pumped into a given mode, which will rapidly saturate unless the energy is leaked to other modes. The latter leakage is presumed to occur extensively at an energy where the density of states is sufficiently large, i.e. where the

so-called quasicontinuum begins (e.g. 183a–c). For some molecules this quasicontinuum is reached already at a very low energy and their absorption cross-section is independent of energy fluence until extensive dissociation is reached (e.g. 184a,b). Thereby, for many molecules there is at least extensive modal-energy mixing at quite low energies. At present it does not appear to be known whether the quantum states involved are chaotic or modal-mixing quasiperiodic. Indeed, the distinction between these may, for some purposes, be unimportant.

Another aspect of whether the quasicontinuum begins at low or at high energies concerns the comparison of the low signal infrared absorption spectrum and the photodissociation spectrum. It has been suggested that if these parallel each other,[6] the quasicontinuum is reached even at the energy at which only one IR quantum is absorbed (e.g. 185, 186a,b). [An alternative interpretation is that there is little or no anharmonic shift. Another interpretation is that only one photon is needed for dissociation, a proposal that can be excluded, since the A–B bond strength is much stronger than the energy of one photon (187)]. Frequently, the photodissociation IR spectrum is red shifted (6) or otherwise rather different from the IR ground state spectrum and the presumption has been that the quasicontinuum does not set in until a higher energy is reached. [For a criticism of that interpretation see review by Lyman (184a) and references cited therein.] In SF_6 a number of absorbed CO_2 photons (e.g. ~ 5) in the ν_3 band are believed needed before the quasicontinuum is reached. A variety of interesting theoretical treatments have been given (cf 6, 188, and references cited therein).

In contrast, van der Waals complexes (8) may provide an example of quasiperiodic states, with their relatively well-defined spectral pattern (8). The large frequency difference between that for the diatomic molecule (I_2 in the I_2He example given earlier) and that for the relative motion ($I_2 \ldots He$) presumably contributes to this stability (24). If the frequencies were similar, about 1:1, or even if they had a low order commensurability, there could be extensive energy exchange between these degrees of freedom, thus leading to a more rapid dissociation.

Fluorescence spectra of rotationally cold molecules have been studied by photoselectively exciting a particular vibration of an electronically excited state, and observing the resulting fluorescence spectrum, e.g. (9a,b). In the case of alkyl benzenes, for the excitation of a particular ring mode (e.g. ν_{6b}), the fluorescence was sharp for short chain alkyl groups but broader for long chain ones. Thus, in the latter case the prepared state, i.e.

[6]In (185, 186a,b) where the dissociation of ions was studied, the photodissociation spectrum was compared with the IR spectrum of the parent molecule, since that of the ion was unknown. For a neutral model see (198).

the set of quantum states excited, in the long chain alkyl case involves a wavepacket of states of different energies, which then dephase. The sharpness of absorption spectra shows that this energy band is very narrow. The diffuseness of the fluorescence spectra shows that even at fairly low energies there is extensive energy randomization. A detailed discussion of the fluorescence spectra, using concepts drawn from electronic relaxation theory, has been given by Freed & Nitzan (189) and, more formally, by Mukamel & Smalley (190). Any dephasing, if it occurs, does so on a time scale less than nanoseconds, the time scale for the time-resolved experiments (9a,b).

Experiments were performed on N_2-alkyl benzene complexes, where the predissociation rate to N_2 and the alkyl benzene was much slower than the fluorescence decay rate for long alkyl chain lengths (191). For argon-alkylbenzene complexes the fluorescence decay rate was much faster than the predissociation rate (191), regardless of chain length. The interpretation of the former is similar to that given above, i.e. the state (or states) prepared by excitation of the ν_6 mode in the excited electronic state is also delocalized in the long chain alkyl benzene.

Energy randomization in the excited electronic state has been studied indirectly by Parmenter and co-workers (10a,b). They examined the fluorescence of *p*-fluorotoluene (and *p*-difluorobenzene) molecules containing about 2000 cm^{-1} vibrational energy in the electronically excited state S_1 using a laser linewidth of 0.3 cm^{-1}. O_2 collisionally quenches the fluorescence. Use of large O_2 pressures reduced the fluorescence to that from molecules living only about 10 ps. The fluorescence became less congested with decreasing survival time for the emitting molecules (increasing O_2 pressure). The results suggest that the combination mode primarily excited is anharmonically coupled to other modes, so that a wavepacket of states is initially formed. The energy differences among the states lead to a "dephasing"; the "dephased state" is a more "randomized state." Its fluorescence is broader than the original. The occurrence of dephasing itself is consistent with the existence of either many quasiperiodic states or chaotic states. A biexponential behavior for the growth of the "unstructured emission" was found, with apparent relaxation times of $\sim$ 10 and $\sim$ 200 ps.

As one might expect in the study of local modes, there is good experimental evidence in the spectrum that one should speak of symmetry-adapted local modes (146). We discuss briefly above the possible transition in the nature of the wavefunction, from that of a normal mode for the fundamental to one of a symmetry adapted local mode for the high overtone case (e.g. in the case of CH vibrations). The origin of the width of these high overtone bands is not yet understood, although some study has

been made (192). Either the width reflects an "energy loss" mechanism to the other modes (T_1 relaxation time) (chaotic or modal mixing quasiperiodic states) or it reflects changes in this CH mode, without energy loss, by coupling to the other modes ("pure T_2" relaxation time) (nonmodal mixing states), the width corresponding to a relaxation time of 1 ps. Trajectory calculations (193) suggest that this mechanism is not of the T_1-type, although such calculations rest of course on an assumed potential energy surface.

There have been laser infrared double resonance investigations, designed to study intramolecular relaxation in vibrationally excited SF_6, by probing different parts of an IR absorption band, one part of which was used to excite the molecule. Lyman (194) has summarized recent studies and the difficulty of determining an intramolecular relaxation time. Other experiments related to intramolecular relaxation are cited in (189).

There have been a number of experimental areas related to intramolecular energy transfer, which, because of space and time limitations, we do not review. These include unimolecular ion decomposition, where the results parallel those found in unimolecular reactions of neutrals, and photodissociation. We refer the reader to recent reviews (195, 196). Other relevant reviews on topics in intramolecular energy transfer are given in (189) and in assorted articles in a recent publication (197).

CONCLUDING REMARKS

Many theoretical studies have provided evidence for a transition in the classical dynamics from largely quasiperiodic behavior at low energies to largely chaotic behavior at high energies. The nature of the corresponding transition in quantum mechanics is being extensively investigated. One possibility (when $\hbar$ is "small enough") involves the transition from a regular to an irregular spectrum, perhaps reflecting the onset of many "avoided" crossings.

Using semiclassical ideas, the correspondence between classical and quantum mechanics is reasonably well understood in the quasiperiodic regime. Mixing of energy in the zeroth order modes can occur even in the quasiperiodic regime via an internal resonance, though in a nonchaotic way. Thus, intramolecular "randomization" of energy can occur both in the chaotic and, particularly when there are enough coordinates, in the quasiperiodic regimes. Thereby, some randomization can arise from an excitation of a wavepacket of many exact quantum states (quasiperiodic or chaotic states) within some energy range in a system with enough coordinates. The subsequent time-evolution of the packet redistributes the energy.

The chance of observing deviations from RRKM-like behavior is presumably greater the narrower the band of states that has been prepared, unless each of those states[7] is chaotic. There is considerable evidence in the experimental data for some randomization, even in the experiments of (9a,b), at low energies in complex molecules. Examples of nonrandomized systems exist (e.g. van der Waals molecules), and the reasons for these probable differences in behavior are beginning to be understood. The challenge to the experimentalist is the preparation of as narrow a band of states as possible, consistent with the study of their real-time evolution. The challenge to both the theorist and the experimentalist is to infer from these data and from high resolution spectroscopic data the nature of the vibrational quantum states involved: in the language of this review, modal-energy-mixing or nonmodal-mixing and, if the former, chaotic or quasiperiodic.

ACKNOWLEDGMENT

We should like to acknowledge helpful discussions during the course of this research with many individuals, including J. R. Stine, R. Ramaswamy, V. K. Babamov, M. Tabor, W. K. Liu, J. D. McDonald, A. H. Zewail, E. A. Jackson, J. L. Beauchamp, and J. L. Lyman. Jim Stine's review of the manuscript was very helpful. A portion of this article was planned while one of us (R.A.M.) was Raymond and Beverly Sackler Distinguished Lecturer at Tel Aviv University. He is particularly grateful to Joshua Jortner, to Matilda Elron, and to their colleagues for their gracious hospitality and stimulating environment. We are most indebted to Joyce Lundstedt for her considerable assistance and for her excellent typing of the manuscript. This research was supported in part by grants from the National Science Foundation and by the US Department of Energy. The article is Contribution No. 6373 from the California Institute of Technology.

Literature Cited

1a. Robinson, P. J., Holbrook, K. A. 1972. *Unimolecular Reactions*. New York: Wiley
1b. Forst, W. 1973. *Unimolecular Reactions*. New York: Academic
2a. Ko, A. N., Rabinovitch, B. S., Chao, K. J. 1977. *J. Chem. Phys.* 66:1374
2b. Hase, W. L. 1976. *Dynamics of Molecular Collisions*, Pt. B, Chap. 3, ed. W. H. Miller. New York: Plenum
3. Farrar, J. M., Lee, Y. T. 1978. *ACS Symp. Ser.* 66:191
4. Miller, W. B., Safron, S. A., Herschbach, D. R. 1972. *J. Chem. Phys.* 56:3581
5a. Ambartzumian, R. V., Letokhov, V. S. 1977. *Chemical and Biochemical Applications of Lasers*, ed. C. B. Moore, 3:1. New York: Academic
5b. Letokhov, V. S. 1977. *Ann. Rev. Phys. Chem.* 28:133
6. Schulz, P. A., Sudbø, Aa. S., Krajnovich, D. J., Kwok, H. S., Shen, Y. R., Lee, Y. T. 1979. *Ann. Rev. Phys.*

[7]All of the "states" in the dissociative region are broadened levels.

Chem. 30:379
7a. Avouris, P., Gelbart, W. M., El-Sayed, M. A. 1977. *Chem. Rev.* 77: 793
7b. Siebrand, W. 1976. *Dynamics of Molecular Collisions,* Pt. A, Chap. 6, ed. W. H. Miller. New York: Plenum
7c. Freed, K. F. 1980. *Adv. Chem. Phys.* 42:207, Sect. 2
7d. Jortner, J., Levine, R. D. 1981. *Adv. Chem. Phys.* 47:1, pt 1
8. Levy, D. H. 1980. *Ann. Rev. Phys. Chem.* 31:197
9a. Hopkins, J. B., Powers, D. E., Smalley, R. E. 1980. *J. Chem. Phys.* 73:683 and refs. cited therein
9b. Beck, S. M., Powers, D. E., Hopkins, J. B., Smalley, R. E. 1980. *J. Chem. Phys.* 73:2019
10a. Dolson, D. A., Parmenter, C. S., Stone, B. M. 1981. *Fast Reactions in Energetic Systems.* NATO Advanced Study Inst. In press
10b. Coveleskie, R. A., Dolson, D. A., Parmenter, C. S. 1980. *J. Chem. Phys.* 72:5774
11. McDonald, J. D. 1979. *Ann. Rev. Phys. Chem.* 30:29
12a. Reddy, K. V., Berry, M. J. 1979. *Faraday Discuss. Chem. Soc.* 67:188
12b. Reddy, K. V., Berry, M. J. 1979. *Chem. Phys. Lett.* 66:223
12c. Cannon, B. D., Crim, F. F. 1980. *J. Chem. Phys.* 73:3013
13a. Henry, B. R. 1977. *Acc. Chem. Res.* 10:207
13b. Fand, H. L., Swofford, R. L. 1980. *J. Chem. Phys.* 73:2607
14. Marcus, R. A. 1952. *J. Chem. Phys.* 20:359
15. Slater, N. B. 1959. *Theory of Unimolecular Reactions.* Ithaca: Cornell Univ. Press
16. Rynbrandt, J. D., Rabinovitch, B. S. 1971. *J. Chem. Phys.* 54:2275
17a. Oref, I., Rabinovitch, B. S. 1979. *Acc. Chem. Res.* 12:166
17b. Wolters, F. C., Rabinovitch, B. S., Ko, A.-N. 1980. *Chem. Phys.* 49:65
18. Hippler, H., Luther, K., Troe, J. 1979. *Faraday Discuss. Chem. Soc.* 67:173
19a. Moser, J. 1973. Stable and random motions in dynamic systems. *Annals of Mathematics Studies,* No. 77. Princeton, NJ: Princeton Univ. Press
19b. Siegel, C. L., Moser, J. L. 1971. *Lectures on Celestial Mechanics.* Berlin: Springer-Verlag
20a. Arnol'd, V. I., Avez, A. 1968. *Ergodic Problems of Classical Mechanics.* New York: Benjamin
20b. Arnol'd, V. I. 1978. *Mathematical Methods of Classical Mechanics.* New York: Springer-Verlag
20c. Ford, J. 1975. *Fundamental Problems in Statistical Mechanics,* ed. E. G. D. Cohen, 3:215. Amsterdam: North Holland
21. Casati, G., Ford, J., eds. 1979. *Stochastic Behavior in Classical and Quantum Hamiltonian Systems. Lecture Notes in Physics,* Vol. 93. *Proc. Volta Mem. Conf. Como, Italy, 1977.* New York: Springer
22. Jorna, S., ed. 1978. *Topics in Nonlinear Dynamics, AIP Conf. Proc.,* No. 46. New York: Am. Inst. Phys.
23. 1980. Articles in *Ann. NY Acad. Sci.* Vol. 37
24. Marcus, R. A. 1977. *Ber. Bunsenges. Phys. Chem.* 81:190
25a. Giacaglia, G. E. O. 1972. *Perturbation Methods in Nonlinear Systems.* New York: Springer-Verlag
25b. Nayfeh, A. H. 1973. *Perturbation Methods.* New York: Wiley
26. Poincaré, H. 1897. *New Methods of Celestial Mechanics.* Transl. NASA, Washington, DC, 1957
27. Fermi, E., Pasta, J., Ulam, S. 1955. *Studies of Nonlinear Problems.* Sci. Rep. LA-1940, Los Alamos Sci. Lab., Los Alamos, N. Mex.
28. Hénon, M., Heiles, C. 1964. *Astron. J.* 69:73
29. Contopoulos, G., Moutsoulas, M. 1965. *Astron. J.* 70:817
30a. Jeffreys, W. H. 1966. *Astron. J.* 71: 306
30b. Barbanis, B. 1966. *Astron. J.* 71:415
31a. Hall, J. L., Carlsten, J. L., eds. 1977. *Laser Spectroscopy III.* New York: Springer
31b. Walther, H., Rothe, K. W., eds. 1979. *Laser Spectroscopy IV.* New York: Springer
32. Visscher, W. H. 1979. *Meth. Comput. Phys.* 15:371
33. Bartlett, J. H. 1975. *Classical and Modern Mechanics.* University Ala: Univ. Alabama Press
34. Swinney, H. L., Gollub, J. P., eds. 1980. *Hydrodynamic Instabilities and the Transition to Turbulence.* Heidelberg: Springer-Verlag
35. Balescu, R. 1975. *Equilibrium and Nonequilibrium Statistical Mechanics.* New York: Wiley
36. Noid, D. W., Koszykowski, M. L., Marcus, R. A. 1977. *J. Chem. Phys.* 67:404
37. Marcus, R. A., Noid, D. W., Koszykowski, M. L. 1979. See Ref. 21, p. 283
38a. Noid, D. W., Koszykowski, M. L.,

Tabor, M., Marcus, R. A. 1980. *J. Chem. Phys.* 72:6169
38b. Noid, D. W., Koszykowski, M. L., Marcus, R. A. 1981. *Classical, Semiclassical and Quantum Mechanical Problems in Mathematics, Chemistry and Physics*, eds. K. Gustavson, W. P. Reinhardt, p. 133. New York: Plenum
39a. Hansel, K. D. 1978. *Chem. Phys.* 33: 35
39b. Hansel, K. D. 1979. *Laser Induced Processes in Molecules*, ed. K. L. Kompa, S. D. Smith, p. 145. New York: Springer-Verlag
40. Powell, G. E., Percival, I. C. 1979. *J. Phys. A* 12:2053
41. Koszykowski, M. L., Noid, D. W., Tabor, M., Marcus, R. A. 1981. *J. Chem. Phys.* 74:2530
42. Mazur, P., Montroll, E. 1960. *J. Math. Phys.* 1:70
43a. Walker, G. H., Ford, J. 1969. *Phys. Rev.* 188:416
43b. Ford, J., Lunsford, G. H. 1970. *Phys. Rev. A* 1:59
44. Ford, J. 1973. *Adv. Chem. Phys.* 24: 155
45. Kolmogorov, A. 1954. *Dokl. Akad. Nauk SSSR* 98:527
46a. Benettin, G., Galgani, L., Strelcyn, J. M. 1976. *Phys. Rev. A* 14:2338
46b. Benettin, G., Froeschle, C., Scheidecker, J. P. 1979. *Phys. Rev. A* 19: 2454
46c. Casartelli, M., Diana, E., Galgani, L., Scotti, A. 1976. *Phys. Rev. A* 13:1921
47a. Chirikov, B. V., Keil, E., Sessler, A. M. 1971. *J. Stat. Phys.* 3:307
47b. Chirikov, B. V., Izrailev, F. M., Tayursky, V. A. 1973. *Comput. Phys. Commun.* 5:11
47c. Zaslavskii, G. M., Chirikov, B. V. 1972. *Sov. Phys. Usp.* 14:549
48a. Noid, D. W. 1976. PhD thesis. Univ. Ill., Urbana
48b. Koszykowski, M. L. 1978. PhD thesis. Univ. Ill., Urbana
49. Oxtoby, D. W., Rice, S. A. 1976. *J. Chem. Phys.* 65:1676
50. Bunker, D. L. 1964. *J. Chem. Phys.* 40:1946
51. Toda, M. 1974. *Phys. Lett. A* 48:335
52a. Brumer, P., Duff, J. W. 1976. *J. Chem. Phys.* 65:3566
52b. Brumer, P. 1981. *Adv. Chem. Phys.* 47:201
53. Cerjan, C., Reinhardt, W. P. 1979. *J. Chem. Phys.* 71:1819
54. Benettin, G., Brambilla, R., Galgani, L. 1977. *Physica A* 87:381
55. Aizawa, Y. 1972. *J. Phys. Soc. Jpn.* 33:1693
56. Noid, D. W., Koszykowski, M. L., Marcus, R. A. 1979. *J. Chem. Phys.* 71:2864
57. Mo, K. C. 1972. *Physica* 57:445
58. Lonke, A., Caboz, R. 1979. *Physica A* 99:350
59a. Mori, H. 1965. *Prog. Theor. Phys.* 33:423
59b. Zwanzig, R. 1960. *Lectures in Theoretical Physics*, ed. W. Britten, B. Down, J. Downs, Vol. 3. New York: Interscience
60. Koszykowski, M. L. Unpublished
61. Ramaswamy, R., Marcus, R. A. 1981. *J. Chem. Phys.* 74:1385
62a. Froeschlé, C. 1971. *Astrophys. Space Sci.* 14:110
62b. Froeschlé, C., Scheidecker, J. P. 1973. *Astrophys. Space Sci.* 25:373
63a. Contopoulos, G., Galgani, L., Giorgilli, A. 1978. *Phys. Rev. A* 18:1183
63b. Carotta, M. C., Ferrario, C., Lo Vecchio, G., Galgani, L. 1978. *Phys. Rev. A* 17:786
64. Tabor, M. 1981. *Adv. Chem. Phys.* 46:73
65. Berry, M. V. 1978. See Ref. 22, p. 16; Berry, M. V. 1980. *Ann. NY Acad. Sci.* 357:169
66. Born, M. 1927. *Mechanics of the Atom*. London: Bell
67. Einstein, A. 1917. *Verh. Dtsch. Phys. Ges.* 19:82
68a. Keller, J. B. 1958. *Ann. Phys.* 4:180
68b. Keller, J. B., Rubinow, S. I. 1960. *Ann. Phys.* 9:24
69. Maslov, V. P. 1962. *Comp. Math. and Math. Phys.* 1:123
70. Marcus, R. A. 1973. *Faraday Discuss. Chem. Soc.* 55:34
71. Eastes, W., Marcus, R. A. 1974. *J. Chem. Phys.* 61:4301
72. Noid, D. W., Marcus, R. A. 1975. *J. Chem. Phys.* 62:2119
73. Noid, D. W., Marcus, R. A. 1977. *J. Chem. Phys.* 67:559
74. Noid, D. W., Koszykowski, M. L., Marcus, R. A. 1980. *J. Chem. Phys.* 73:391
75. Noid, D. W., Koszykowski, M. L. 1980. *Chem. Phys. Lett.* 73:114
76a. Percival, I. C., Pomphrey, N. 1976. *Mol. Phys.* 31:97
76b. Percival, I. C., Pomphrey, N. 1976. *J. Phys. B* 9:3131
76c. Percival, I. C. 1977. *Adv. Chem. Phys.* 36:1
77. Percival, I. C., Pomphrey, N. 1978. *Mol. Phys.* 35:649
78a. Leopold, J. G., Percival, I. C. 1980. *J. Phys. B* 13:1037
78b. Leopold, J. G., Percival, I. C., Twor-

kowski, A. S. 1980. *J. Phys. B* 13: 1025
79. Jaffé, C., Reinhardt, W. P. 1979. *J. Chem. Phys.* 71:1862
80. Colwell, S. M. 1980. *Chem. Phys.* 46: 165
81. Chapman, S., Garrett, B. C., Miller, W. H. 1976. *J. Chem. Phys.* 64:502
82. Handy, N. C., Colwell, S. M., Miller, W. H. 1977. *Faraday Discuss. Chem. Soc.* 62:29
83a. Sorbie, K. S. 1976. *Mol. Phys.* 32: 1577
83b. Sorbie, K. S., Handy, N. C. 1977. *Mol. Phys.* 33:1319
84. Sorbie, K. S., Handy, N. C. 1976. *Mol. Phys.* 32:1327
85. Colwell, S. M., Handy, N. C. 1978. *Mol. Phys.* 35:1183
86. Handy, N. C. 1980. *Semiclassical Methods in Molecular Scattering and Spectroscopy, NATO Adv. Study Inst. Ser. C: Math. Physical Sci.*, ed. M. S. Child, p. 297. Dordrecht: Reidel
87a. Delos, J. B., Swimm, R. T. 1977. *Chem. Phys. Lett.* 47:76
87b. Swimm, R. T., Delos, J. B. 1979. *J. Chem. Phys.* 71:1706
87c. Swimm, R. T., Delos, J. B. 1979. See Ref. 21, p. 306
88. Birkoff, G. D. 1966. *Dynamical Systems.* New York: Am. Math. Soc.
89. Gustavson, F. G. 1966. *Astron. J.* 71: 670
90a. Siegal, C. L. 1941. *Ann. Math.* 42:806
90b. Siegal, C. L. 1945. *Math. Ann.* 128: 144
90c. Siegal, C. L., Moser, J. L. See Ref. 19, Sect. 30
91. Jaffé, C. 1979. PhD thesis. Univ. Colo., Boulder
92. Schatz, G. C., Moser, M. D. 1978. *Chem. Phys.* 35:239
93. Schatz, G. C., Mulloney, T. 1979. *J. Phys. Chem.* 83:989
94. Ramaswamy, R., Siders, P., Marcus, R. A. 1980. *J. Chem. Phys.* 73:5400
95. Gutzwiller, M. C. 1967. *J. Math. Phys.* 8:1979
96. Gutzwiller, M. C. 1970. *J. Math. Phys.* 11:1971; Gutzwiller, M. C. 1979. See Ref. 21, p. 316
97. Gutzwiller, M. C. 1969. *J. Math. Phys.* 10:1004
98. Gutzwiller, M. C. 1971. *J. Math. Phys.* 12:343
99. Gutzwiller, M. C. 1980. *Phys. Rev. Lett.* 45:150
100. Miller, W. H. 1972. *J. Chem. Phys.* 56:38
101. Miller, W. H. 1975. *J. Chem. Phys.* 63:996
102. Berry, M. V., Tabor, M. 1976. *Proc. R. Soc. London Ser. A* 349:101
103a. Berry, M. V., Tabor, M. 1977. *J. Phys. A* 10:371
103b. Tabor, M. 1979. See Ref. 21, p. 293
104. Gerber, R. B., Ratner, M. A. 1979. *Chem. Phys. Lett.* 68:195
105. Berry, M. V. 1980. *Ann. Phys. NY* 131:163
106a. Nordholm, K. S. J., Rice, S. A. 1974. *J. Chem. Phys.* 61:203
106b. Nordholm, S., Rice, S. A. 1974. *J. Chem. Phys.* 61:768
106c. Nordholm, S., Rice, S. A. 1975. *J. Chem. Phys.* 62:157
107. Heller, E. J. 1979. *Chem. Phys. Lett.* 60:338
108. Kosloff, R., Rice, S. A. 1980. *Chem. Phys. Lett.* 69:209
109. Stratt, R. M., Handy, N. C., Miller, W. H. 1979. *J. Chem. Phys.* 71:3311
110. Kay, K. G. 1980. *J. Chem. Phys.* 72: 5955
111a. Percival, I. C. 1973. *J. Phys. B* 6: L229
111b. Pomphrey, N. 1974. *J. Phys. B* 7: 1909
112. McDonald, S. W., Kaufman, A. N. 1979. *Phys. Rev. Lett.* 42:1189
113. Berry, M. V., Tabor, M. 1977. *Proc. R. Soc. London Ser. A* 356:75
114. Zaslavskii, G. M. 1977. *Sov. Phys. JETP* 46:1094
115. Wigner, E. P. 1932. *Phys. Rev.* 40: 749
116. Wigner, E. P. 1967. *SIAM Rev.* 9:1
117. Casati, G., Valz-Gris, F., Guarnieri, I. 1980. *Lett. Nuovo Cimento* 28:279
118. Bunimovich, L. A. 1974. *Funct. Anal. Appl.* 8:254
119. Berry, M. V. 1977. *Philos. Trans. R. Soc. London Ser. A* 287:237
120. Berry, M. V. 1977. *J. Phys. A* 10: 2083
121. Hutchinson, J. S., Wyatt, R. E. 1980. *Chem. Phys. Lett.* 72:378
122. Brumer, P., Shapiro, M. 1980. *Chem. Phys. Lett.* 72:528
123. Kosloff, R., Rice, S. A. 1981. *J. Chem. Phys.* 74:1340
124. Heller, E. J. 1980. *Chem. Phys. Lett.* 76:21
125. Weissman, Y., Jortner, J. 1981. *Chem. Phys. Lett.* 78:224
126. Heller, E. J. 1980. *J. Chem. Phys.* 72: 1337
127. Noid, D. W., Koszykowski, M. L., Marcus, R. A. 1980. *Chem. Phys. Lett.* 73:269
128. Marcus, R. A. 1980. *Horizons in Quantum Chemistry*, ed. K. Fukui, B. Pullman, p. 107. Dordrecht: Reidel

129. Marcus, R. A. 1980. *Ann. NY Acad. Sci.* 357:159
130. Neuberger, J. W., Noid, D. W., Marcus, R. A. Unpublished
131. Ramaswamy, R., Marcus, R. A. 1981. *J. Chem. Phys.* 74:1379
132a. Berry, M. V., Balazs, N. L., Tabor, M., Voros, A. 1979. *Ann. Phys. NY* 122:26
132b. Tabor, M. 1981. *Classical, Semiclassical and Quantum Mechanical Problems in Mathematics, Chemistry and Physics,* ed. K. Gustavson, W. P. Reinhardt. New York: Plenum Press. In press
133. Berman, G. P., Zaslavsky, G. M. 1978. *Physica A* 91:450
134. Casati, G., Chirikov, B. V., Izrailev, F. M., Ford, J. 1979. See Ref. 21, p. 334
135. Dirac, P. A. M. 1958. *The Principles of Quantum Mechanics.* London: Oxford Univ. Press. 4th ed.
136. Ramaswamy, R., Marcus, R. A. Unpublished
137a. Moser, J. 1978. See Ref. 22, p. 1
137b. Arnol'd, V. I. 1978. See Ref. 20b, p. 272
138. Gutzwiller, M. C. 1980. *Ann. Phys. NY* 124:347
139. Noid, D. W., Koszykowski, M. L., McDonald, J. D., Marcus, R. A. Unpublished
140. Shuryak, E. V. 1977. *Sov. Phys. JETP* 44:1070
141. Koszykowski, M. L., Noid, D. W., Marcus, R. A. To be published
142a. Kulander, K. C., Heller, E. J. 1978. *J. Chem. Phys.* 69:2439
142b. Heller, E. J., Stechel, E. B., Davis, M. J. 1980. *J. Chem. Phys.* 73:4720
143. Abarbanel, H. D. I., Crawford, J. D. 1981. *Phys. Lett. A* 82:378
144a. Hayward, R. J., Henry, B. R. 1974. *J. Mol. Spectrosc.* 50:58
144b. Swofford, R. L., Long, M. E., Albrecht, A. C. 1976. *J. Chem. Phys.* 65:179
144c. Perry, J. W., Zewail, A. H. 1979. *J. Chem. Phys.* 70:582
144d. Bray, R. G., Berry, M. J. 1979. *J. Chem. Phys.* 71:4909
145a. Lawton, R. T., Child, M. S. 1979. *Mol. Phys.* 37:1799
145b. Lawton, R. T., Child, M. S. 1980. *Mol. Phys.* 40:773
146a. Perry, J. W., Zewail, A. H. 1981. *J. Phys. Chem.* 85:933
146b. Waite, B. A., Miller, W. H. 1981. *J. Chem. Phys.* 74:3910
147a. Bunker, D. L. 1977. *Ber. Bunsenges. Phys. Chem.* 81:155
147b. Bunker, D. L. 1974. *Acc. Chem. Res.* 7:195
148. Bunker, D. L., Hase, W. L. 1973. *J. Chem. Phys.* 59:4621 and refs. cited therein
149a. Baetzold, R. C., Wilson, D. J. 1965. *J. Chem. Phys.* 43:4299
149b. Thiele, E. 1963. *J. Chem. Phys.* 38: 1959
150a. Wolf, R. J., Hase, W. L. 1980. *J. Chem. Phys.* 73:3779 and refs. cited therein
150b. Hase, W. L. 1980. *Chem. Phys. Lett.* 67:263
151. Brumer, P., Karplus, M. 1973. *Discuss. Faraday Soc.* 55:80
152. Parr, C. A., Kuppermann, A., Porter, R. N. 1977. *J. Chem. Phys.* 66:2914
153. McDonald, J. D., Marcus, R. A. 1976. *J. Chem. Phys.* 65:2180
154. Woodruff, S. B., Thompson, D. L. 1979. *J. Chem. Phys.* 71:376
155a. Noid, D. W., Koszykowski, M. L., Marcus, R. A., McDonald, J. D. 1977. *Chem. Phys. Lett.* 51:540
155b. Marcus, R. A., Noid, D. W., Koszykowski, M. L. 1978. *Advances in Laser Chemistry,* ed. A. H. Zewail, p. 298. New York: Springer
155c. Noid, D. W., Bottcher, C., Koszykowski, M. L. 1980. *Chem. Phys. Lett.* 72:397
156a. Hansel, K. D. 1978. *Chem. Phys. Lett.* 57:619
156b. Hansel, K. D. 1979. *J. Chem. Phys.* 70:1830
157. Ramaswamy, R., Siders, P., Marcus, R. A. 1981. *J. Chem. Phys.* 74:4418
158. Poppe, D. 1980. *Chem. Phys.* 45:371
159a. Noid, D. W., Stine, J. R. 1979. *Chem. Phys. Lett.* 65:153
159b. Stine, J. R., Noid, D. W. 1979. *Optics Commun.* 31:161
160a. Stine, J. R., Noid, D. W. 1981. *Chem. Phys. Lett.* 77:287
160b. Noid, D. W., Stine, J. R. 1981. *Opt. Commun.* 37:187
161. Schatz, G. C., Mulloney, T. 1979. *J. Chem. Phys.* 71:5257
162a. Noid, D. W., Koszykowski, M. L. 1981. *Chem. Phys. Lett.* 79:45
162b. Noid, D. W., Liu, W. K. 1981. *Chem. Phys.* In press
163. Duff, J. W., Brumer, P. 1977. *J. Chem. Phys.* 67:4898
164a. Hutchinson, J. S., Wyatt, R. E. 1979. *J. Chem. Phys.* 70:3509
164b. Penly, R. T., Hutchinson, J. S., Wyatt, R. E. 1980. *Chem. Phys. Lett.* 69: 255
164c. Hutchinson, J. S., Wyatt, R. E. 1981. *Phys. Rev. A* 23:1567
165. Liu, W. K., Noid, D. W. 1980. *Chem. Phys. Lett.* 74:152

166a. Pechukas, P., Light, J. C. 1965. *J. Chem. Phys.* 42:3281
166b. Keck, J. 1958. *J. Chem. Phys.* 29:410
167. Quack, M., Troe, J. 1974. *Ber. Bunsenges. Phys. Chem.* 78:240
168. Marcus, R. A. 1965. *J. Chem. Phys.* 43:1598
169a. Worry, G., Marcus, R. A. 1977. *J. Chem. Phys.* 67:1636
169b. Marcus, R. A. 1975. *J. Chem. Phys.* 62:1372
170. Schlag, E. W., Rabinovitch, B. S. 1960. *J. Am. Chem. Soc.* 82:5996
171a. Schneider, F. W., Rabinovitch, B. S. 1963. *J. Am. Chem. Soc.* 85:2365
171b. Ravinovitch, B. S., Gilderman, P. W., Schneider, F. W. 1965. *J. Am. Chem. Soc.* 87:158
172. Hsieh, J. C., Huang, C. S., Lim, E. C. 1974. *J. Chem. Phys.* 60:4345
173. Huang, C. S., Hsieh, J. C., Lim, E. C. 1976. *Chem. Phys. Lett.* 37:349
174. Freed, K. F. 1979. *Faraday Discuss. Chem. Soc.* 67:231
175. Moss, M. G., Ensminger, M. D., Stewart, G. M., Mordaunt, D., McDonald, J. D. 1980. *J. Chem. Phys.* 73:1256 and refs. cited therein
176a. Durana, J. F., McDonald, J. D. 1976. *J. Chem. Phys.* 64:2518
176b. Cheung, J. T., McDonald, J. D., Herschbach, D. R. 1973. *J. Am. Chem. Soc.* 95:7889
177. Wolf, R. J., Hase, W. L. 1980. *J. Chem. Phys.* 72:316; 73:3010
178. Moehlmann, J. G., Gleaves, J. T., Hudgens, J. W., McDonald, J. D. 1974. *J. Chem. Phys.* 60:4790
179. Stephenson, J. C., Bialkowski, S. E., King, D. S., Thiele, E., Stone, J., Goodman, M. F. 1981. *J. Chem. Phys.* 74:3905
180. Thiele, E., Goodman, M. F., Stone, J. 1980. *Chem. Phys. Lett.* 69:18
181. Schultz, P. A., Sudbø, Aa. S., Grant, E. R., Shen, Y. R., Lee, Y. T. 1980. *J. Chem. Phys.* 72:4985
182. Richardson, T. H., Setser, D. W. 1977. *J. Phys. Chem.* 81:2301
183a. Bloembergen, N., Yablonovitch, E. 1978. *Phys. Today* 31:33, No. 5
183b. Bloembergen, N. 1975. *Opt. Commun.* 15:416
183c. Lyman, J. L., Danen, W. C., Nilsson, A. C., Nowak, A. V. 1979. *J. Chem. Phys.* 71:1206 and refs. cited therein
184a. Lyman, J. L., Quigley, G. P., Judd, O. P. 1981. *Multiple Photon Excitation and Dissociation of Polyatomic Molecules*, ed. C. Cantrell. Heidelberg: Springer-Verlag
184b. Lyman, J. L., Leary, K. M. 1978. *J. Chem. Phys.* 69:1858
185. Bomse, D. S., Beauchamp, J. L. 1981. *Chem. Phys. Lett.* 77:25
186a. Woodin, R. L., Bomse, D. S., Beauchamp, J. L. 1979. *Chemical and Biological Applications of Lasers*, ed. C. B. Moore, 4:355. New York: Academic
186b. Bomse, D. S., Woodin, R. L., Beauchamp, J. L. 1979. *J. Am. Chem. Soc.* 101:5503
187. Beauchamp, J. Private communication
188. Galbraith, H. S., Ackerhalt, J. R. 1980. *Laser-Induced Processes*, ed. J. Steinfeld, Vol. 1. New York: Plenum
189. Freed, K. F., Nitzan, A. 1980. *J. Chem. Phys.* 73:4765
190. Mukamel, S., Smalley, R. E. 1980. *J. Chem. Phys.* 73:4156
191. Hopkins, J. B., Powers, D. E., Smalley, R. E. 1981. *J. Chem. Phys.* 74: 745
192. Heller, D. F., Mukamel, S. 1979. *J. Chem. Phys.* 70:463
193. Nagy, P. J., Hase, W. L. 1978. *Chem. Phys. Lett.* 54:73
194. Lyman, J. L. 1981. *Molecular Structure and Energy Scrambling*, ed. J. Hinze. Zentrum f. Interdisziplinare Forschung Univ. Bielefeld. New York: Plenum
195. Rice, S. A. 1975. *Excited States*, ed. E. C. Lim, 2:111. New York: Academic
196. Brenton, A. G., Morgan, R. P., Beynon, J. H. 1979. *Ann. Rev. Phys. Chem.* 30:51
197. Zewail, A. H., Letokhov, V. S., Zare, R. N., Bernstein, R. B., Lee, Y. T., Shen, Y. R. 1980. *Phys. Today* 33:25, No. 11
198. Hudgens, J. W., McDonald, J. D. 1981. *J. Chem. Phys.* 74:1510