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INTERNAL ENERGY TRANSFER IN ISOLATED MOLECULES: ERGODIC AND NON--ETC(U)
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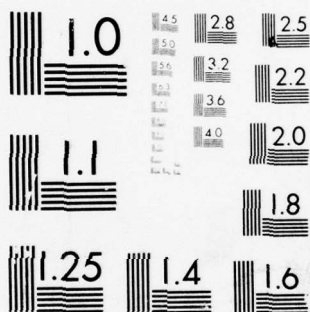
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19. REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR-TR-79-0797	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) INTERNAL ENERGY TRANSFER IN ISOLATED MOLECULES: ERGODIC AND NONERGODIC BEHAVIOR		5. TYPE OF REPORT & PERIOD COVERED Interim report
6. AUTHOR(s) Stuart A. Rice		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS The James Franck Institute The University of Chicago Chicago, Illinois 60637		8. CONTRACT OR GRANT NUMBER(s) F49620-76-C-0017
11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research (NC) Building 410 Bolling AFB, D. C. 20332		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 61102F 2303/B1
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) LEVEL		12. REPORT DATE 1978
		13. NUMBER OF PAGES 43
		15. SECURITY CLASS. (of this report) Unclassified
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES ADVANCES IN LASER CHEMISTRY 3, p 2-42, 1978.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) ergodic theory energy transfer quasi-periodic motion intramolecular energy		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) This paper addresses the following questions: (1) Under what conditions, if any, is intramolecular energy exchange slow/rapid relative to other processes, for example photon emission, or isomerization, or fragmentation? 2) How does the intramolecular energy exchange depend on the energy of the molecule and the nature of the initial excitation? (3) If there are situations for which intramolecular energy exchange is slow relative to chemical reaction, why does this behavior occur? Does it derive from special characteristics of the molecular force fields? Are there dynamical or symmetry restrictions on the		

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INTERNAL ENERGY TRANSFER IN ISOLATED MOLECULES:
ERGODIC AND NONERGODIC BEHAVIOR

Stuart A. Rice

The Department of Chemistry and The James Franck Institute
The University of Chicago
Chicago, Illinois 606371. Introduction

I have been asked to present a broad overview of current understanding of the nature of intramolecular energy transfer in isolated molecules. In the short time available for this talk I can do no more than describe very briefly some attempts to answer the major questions associated with this subject. In my opinion these are:

1. Under what conditions, if any, is intramolecular energy exchange slow/rapid relative to other processes, for example photon emission, or isomerization, or fragmentation?
2. How does the intramolecular energy exchange depend on the energy of the molecule and the nature of the initial excitation?
3. If there are situations for which intramolecular energy exchange is slow relative to chemical reaction, why does this behavior occur? Does it derive from special characteristics of the molecular force fields? Are there dynamical or symmetry restrictions on the spectrum of states in these cases? Are these special situations commonly or rarely found?
4. Given the answers to (3), can we devise excitation methods and reaction conditions that permit enhancement of the selectivity of the chemistry that follows?

These questions are pertinent to all types of reaction dynamics. They are raised at a conference devoted to laser chemistry because the laser provides a tool with which one can construct experiments that attempt to answer them. Prior to the development of laser sources suitable for the preparation of isolated molecules in well defined non-stationary states these questions could not be addressed. The kinds of phenomena associated with the decay of incoherent superpositions of molecular states, such as is characteristic of thermal energization of a molecule, are naturally and elegantly described by statistical theories. The RRKM theory [1], which successfully accounts for the rates of thermal unimolecular reactions and the vast majority of chemically activated unimolecular reactions, is a brilliant example of appropriate analysis. But the very success of statistical theories has led to a too ready acceptance of their applicability to situations different from the ones they were designed to describe. For example, one of the most widely held of the current views concerning intramolecular dynamics is that vibrational relaxation is always rapid relative to all other processes except for energies near the ground state. Furthermore, it is often assumed that the rapid randomization of vibrational energy follows automatically from the existence of anharmonicity.

The consensus concerning this assumption can be traced to the notion that it is implied by the success of RRKM theory in the description of thermal unimolecular reactions. But the data for thermal unimolecular reactions rarely require such an interpretation because of the incoherent nature of the initial thermal excitation. Chemical activation of unimolecular reactions in bulk experiments suffers from similar, but not as severe difficulties of interpretation vis a vis the initial state of excitation. The point is not that intramolecular vibrational energy exchange does not occur in these cases, but rather that determining whether it does or does not occur cannot be uniquely inferred. Evidence that randomization of vibrational energy may not always be faster than other processes is inferred from several different kinds of experiments on isolated molecules [2]. However, all of the inferences are indirect and they are based on the use of extra assumptions in the analysis of the observations, hence they can be erroneous [3]. Similarly, although many theoretical models show that vibrational relaxation can in certain circumstances be very slow compared to other processes [4], these models employ simplifications that reduce their applicability to real molecular systems. In short, there are now a number of hints, from both experimental and theoretical studies, that suggest the existence of some cases for which vibrational energy redistribution is slower than other processes. The conditions for which this slow relaxation occurs, its generality, and its relation to molecular structure are not known. Even the existence of the phenomenon in real molecules is not unequivocally established because of inadequacies in experimental design, approximations in the interpretation of observations, and simplifications employed in the theoretical models. Despite these caveats, it is possible to assert with assurance that there is not a universal form of statistical behavior characteristic of all energized molecules. The picture which is emerging requires recognition of the existence of different dynamical domains, each of which is important in a different energy range and on a different time scale. As I shall show, there is little doubt that up to about one half or two thirds of a typical bond dissociation energy a molecule is not well described by a statistical model, whereas for larger energies the statistical model is accurate for many purposes. In addition, even when the energy of the molecule exceeds, say, a bond dissociation energy, if there are processes sufficiently fast to compete with energy randomization, deviations from statistical behavior are to be expected. Although this statement is *prima facie* obvious, the acceptance of the notion that there might exist processes that can compete with energy randomization, or that energy randomization can be as slow as hundreds of vibrational periods, has only recently been accepted as a necessary part of the description of reaction dynamics.

The brief discussion of the following sections is intended to draw attention to several of the subtleties in the behavior of systems of coupled nonlinear oscillators. Wherever possible, both classical and quantum mechanical models are considered. After surveying the various theoretical predictions it will be argued that some of the dynamical properties discovered in simple models are, in fact, robust, and are important for understanding intramolecular vibrational relaxation and reaction dynamics in real systems.

II. A Few Properties of Nonlinear Dynamical Systems

Any discussion of intramolecular dynamics of highly excited molecules must confront the problem of describing large amplitude motions of the atoms. It is a cliché, though true, that most of our intuitive sense for how systems of oscillators should behave is derived from examples for which a linear analysis or a perturbation to a linear analysis is possible, e.g. harmonic motion or weakly coupled harmonic motion. While this way of thinking suffices for the description of small amplitude motions of the atoms of a molecule, it is inapplicable to the description of large amplitude motions. The point is that the nonlinearities of the restoring force field are so important that the dynamics can be qualitatively different from that predicted by extrapolation from the harmonic limit. For example, it is not possible to predict the existence of solitary waves on a chain of nonlinear oscillators with a perturbation theory analysis starting from the harmonic oscillator limit [5]. The existence of qualitatively new phenomena in the large amplitude limit suggests we rethink our analyses of intramolecular vibrational dynamics. It is not yet established that these special large amplitude phenomena have important chemical consequences, but the hint that they are important is strong.

The remarkable developments of the past two decades in the analysis of nonlinear dynamical systems are not widely known to chemists. For that reason I will presume on your patience and sketch some of the ideas and results that appear to bear on the rate of intramolecular vibrational relaxation, and its coupling to other processes.

I shall discuss the classical mechanical case first, and then the quantum mechanical case.

A. Some Properties of Trajectories (CM) [6]

Given a dynamical system with N degrees of freedom described by the Hamiltonian $H(p, q)$ and the equations of motion

$$\dot{q}_s = \frac{\partial H}{\partial p_s}, \quad \dot{p}_s = -\frac{\partial H}{\partial q_s}, \quad (1)$$

and given the initial values of the coordinates and momenta, q_s^0, p_s^0 the values of q, p at any other time t

$$q_s = q_s(t, q^0, p^0), \quad p_s = p_s(t, q^0, p^0), \quad (2)$$

are unique under very weak conditions. Eqs. (2) can in principle, be solved for q_s^0, p_s^0 ,

$$q_s^0 = q_s^0(t, q, p), \quad p_s^0 = p_s^0(t, q, p), \quad (3)$$

which gives $2N$ functions of the phase space variables and the time which are constant along any trajectory of the system. Elimination of t between the equations (3) leaves $2N-1$ functions of only the phase space variables; these functions also have the property of being constant along any trajectory. This argument establishes the existence of $2N-1$ functions $\mathcal{C}_j(q, p)$ which are integrals of the motion; attributing a set of numerical values to the $\mathcal{C}_j$ is equivalent to completely determining the system

trajectory in phase space.

Saying that the set of $2N-1$ values of $\mathcal{C}_j$ determine the trajectory is one thing; finding the values is quite another! Of course, every constant of the motion must satisfy the Poisson-Bracket relation

$$\{H, \mathcal{C}_j\} = 0, \quad j=1, 2, \dots, 2N-1 \quad (4)$$

but the only obvious solution is $\mathcal{C}_1 = H(q, p)$. Although it is in principle possible to stepwise find $2N-2$ other functions which with $\mathcal{C}_1$ form a complete set of functionally independent integrals of the motion, in practice this is impossible to execute even for very simple mechanical systems.

Note that $\mathcal{C}_1 = H$ requires that the trajectory of a conservative system lie on the energy surface $H(q, p) = E$. In general, each of the equations

$$\mathcal{C}_j = k_j \quad j=1, 2, \dots, N-1 \quad (5)$$

for given k_j defines a $2N-1$ dimensional hypersurface in the $2N$ dimensional phase space. The trajectory of the system must lie entirely on each of these surfaces, hence is determined entirely by their hyperdimensional intersection. Put in slightly different words, fixing the value of any $\mathcal{C}_j$ restricts the region of phase space in which the trajectory can lie. Specification of all $2N-1$ $\mathcal{C}_j$ reduces the allowable dimensionality from $2N$ to 1, which is the trajectory of the system. However, the integrals of the motion $\mathcal{C}_j$ are of two types. Some are isolating, in the sense that the domain of phase space to which they restrict the trajectory is compact and readily partitioned from the full phase space-- the language used here is loose but the geometric visualization intended should be clear. The integral $\mathcal{C}_1 = H(q, p)$ is of this type. Others, apparently the vast majority, are nonisolating. The regions of phase space to which they restrict the trajectory pass tortuously through the full domain accessible under the isolating integrals of motion. The distinction between these two classes of integrals of the motion is evident even for the simple system of two independent harmonic oscillators whose Hamiltonian is, of course ($m=1$),

$$H = \frac{1}{2}(\dot{p}_1^2 + \omega_1^2 q_1^2) + \frac{1}{2}(\dot{p}_2^2 + \omega_2^2 q_2^2), \quad (6)$$

which leads to the equations of motion

$$\left. \begin{aligned} \dot{p}_i \cos \omega_i t + \omega_i q_i \sin \omega_i t &= \dot{p}_i^0 \\ \omega_i q_i \cos \omega_i t - \dot{p}_i \sin \omega_i t &= \omega_i q_i^0 \end{aligned} \right\} \quad i=1, 2. \quad (7)$$

Elimination of t , for each value of i , gives

$$\left. \begin{aligned} \dot{p}_i^2 + \omega_i^2 q_i^2 &= \dot{p}_i^{02} + \omega_i^2 q_i^{02} = \text{constant} \\ \mathcal{C}_i &= \frac{1}{2}(\dot{p}_i^2 + \omega_i^2 q_i^2) \end{aligned} \right\} \quad i=1, 2. \quad (8)$$

Finally, elimination of t between the equations of motion for different $i = 1, 2$ leads to a third integral of the motion, $\mathcal{C}_3$. The nature of $\mathcal{C}_3$ depends on the ratio ω_2/ω_1 , in particular on whether this ratio is rational or irrational. In the case that ω_2/ω_1 is rational the projection of the system trajectory on the q_1, q_2 plane is a closed curve, in fact a Lissajous figure. In this case $\mathcal{C}_3(q, p)$ is a multivalued function with a finite number of branches. On the other hand, if ω_2/ω_1 is irrational, the projection of the system trajectory on the q_1, q_2 plane does not generate a closed curve because there can be no rational integer set which leads to matching of the periods of the two oscillators. As a result, the motion of the system is not periodic, and the projected trajectory in the q_1, q_2 plane passes arbitrarily close to each point lying within the rectangle defined by the maximum amplitudes of the two oscillators. The trajectory thereby densely fills the accessible q_1, q_2 space. Although the integral of the motion on $\mathcal{C}_3$ exists, it is a pathological function, namely a multivalued function with an infinite number of branches. Note that when ω_2/ω_1 is rational, the projected trajectory is a Lissajous figure that restricts the motion of the representative point to a small portion of the q_1, q_2 plane. In this case $\mathcal{C}_3$ is an isolating integral of the motion. But when ω_2/ω_1 is irrational the existence of $\mathcal{C}_3$ does not prevent the projected trajectory from filling the energetically accessible region of the q_1, q_2 plane. In this latter case $\mathcal{C}_3$ is a nonisolating integral of the motion.

A different view of dynamics is given by the Hamilton-Jacobi form of mechanics. This representation of the dynamics is based on finding a canonical transformation such that

$$K = H(P), \quad \dot{Q}_s = \frac{\partial K}{\partial P_s} = \omega_s(P), \quad \dot{P}_s = -\frac{\partial K}{\partial Q_s} = 0. \quad (9)$$

The new momenta P_s are integrals of the motion, while the new coordinates Q_s are linear functions of time. Note that only N constants of the motion are determined by the canonical transformation, so the system trajectory is restricted to an $N - 1$ dimensional subspace of the full phase space, but not to a smaller space. For a bounded system linear combinations of the P_s define actions $\mathcal{J}_s$ and their conjugate angle variables ϕ_s ; the $\mathcal{J}_s$ and ϕ_s define the action-angle representation of mechanics. It is only for the case of a system of independent hermanic oscillators that the ω_s are independent of P_s and constant. In more general cases we can, in principle, find $H(\mathcal{J}, \phi)$ but the corresponding frequencies will not be independent of $\mathcal{J}$.

Consider the situation in which the system Hamiltonian can be separated into

$$H(\mathcal{J}, \phi) = H_0(\mathcal{J}) + \lambda H_1(\mathcal{J}, \phi). \quad (10)$$

$H_0(\mathcal{J})$ describes an integrable system, the trajectories of which densely cover regions of phase space. As in the example of two harmonic oscillators with ω_2/ω_1 irrational, we expect that when regions of phase space are densely covered the frequencies $\omega_i \equiv (\partial H_0 / \partial \mathcal{J}_i)$ are not related by a set of rational integers. The term $\lambda H_1(\mathcal{J}, \phi)$ is a "small" perturbation. The traditional view of the influence of anharmonicity on the motion of coupled oscillators suggests that λH_1 destroys the topological structure of the trajectories corresponding to $H_0(\mathcal{J})$ no matter how small λH_1 , if only enough

time elapses. The idea is that λH_1 causes the trajectory to wander out of densely filled regions corresponding to $H_0(\mathcal{J}) = \text{constant}$, thereby filling all of accessible phase space.

A remarkable theorem, due to Kolmogoroff, Arnold and Moser (KAM) [7], implies that the intuitive description of the trajectory just given is incorrect. The theorem says that provided λ is "sufficiently small" and $H_1(\mathcal{J}, \phi)$ is analytic in $\mathcal{J}$ and ϕ in a given domain, the phase space can be separated into two regions of nonvanishing volume. One of these is small, and it shrinks to zero volume as $\lambda \rightarrow 0$. The larger of the two regions has the structure characteristic of $H_0(\mathcal{J})$. Thus, the KAM theorem asserts that for the majority of initial conditions the trajectories of the system have the same character as in the uncoupled oscillator case (Lissajous figures restricted to N-1 dimensions). There is a small region (of instability) in which the trajectories are wildly erratic and can depart drastically from the nearby confined trajectories.

To apply the KAM theorem we need to know what is "small enough" with respect to λ or, equivalently, for fixed λ how the topological behavior of the trajectory changes as the energy of the system increases. At present all of our knowledge concerning this crucial point is derived from numerical solutions of the equations of motion of model systems [8]. Some hypotheses, based on analytical considerations, have been advanced to explain the results of the numerical studies [9], [10], [11], but these have followed and cannot yet replace the trajectory calculations.

In a sense, it can be said that numerical solution of the equations of motion of some system is intended to reveal the consequences of the breakdown of integrability and the lack of isolating integrals of the motion other than the energy. Poincaré [12] introduced a representation of the results of trajectory analysis which permits visualization of these consequences. This representation, which is most useful for two dimensional systems, portrays the motion on a so-called (Poincaré) surface of section. Consider, for simplicity, a Hamiltonian of the form ($m = 1$)

$$H = \frac{1}{2} (p_1^2 + p_2^2) + f(q_1, q_2). \quad (11)$$

For fixed energy, $H = E$, (11) has only three independent variables. One surface of section is defined by the intersection of $H = E$ with $q_1 = 0$; in that plane the coordinates are p_2 and q_2 . To each point in the surface of section there corresponds a unique value of p_2 and q_2 , and of E and $q_1 = 0$. Then p_1 is determined except for sign since, from (11),

$$p_1 = \pm [2E - p_2^2 - f(q_2, 0)]^{1/2}. \quad (12)$$

A given trajectory of a bound system will repeatedly cross the surface of section, since that trajectory must repeatedly pass through $q_1 = 0$, half the passages with $p_1 > 0$ and half with $p_1 < 0$. We now recognize two possibilities. If there exist isolating integrals of the motion other than the energy, such as $\mathcal{C}_3$ with ω_2/ω_1 rational for the Hamiltonian (6), the system trajectory lies on a hypersurface of smaller dimensionality

than the energy surface. This hypersurface intersects the surface of section in a smooth closed curve -- closed because the motion is periodic. In contrast, if there is not any isolating integral of the motion other than the energy, the intersections of the trajectory with the surface of section will cover that surface. The pattern of intersections will appear random, but is in fact not, since the trajectory satisfies the deterministic equation of motion. The two cases described are schematically sketched in Fig. 1.

To illustrate both the subtleties of nonlinear mechanics and the consequences of the KAM theorem consider the Toda Hamiltonian [13]

$$H(q, p) = \frac{1}{2} (p_1^2 + p_2^2) + \frac{1}{24} [e^{2q_2 + 2\sqrt{3}q_1} + e^{2q_2 - 2\sqrt{3}q_1} + e^{-4q_2}] - \frac{1}{8}, \quad (13)$$

and that generated by expanding (13) to third order in q_1 and q_2 , known as the Henon-Heiles Hamiltonian [14],

$$H(q, p) = \frac{1}{2} (p_1^2 + p_2^2) + \frac{1}{2} (q_1^2 + q_2^2) + q_1^2 q_2 - \frac{1}{3} q_2^3. \quad (14)$$

The trajectories corresponding to (13) were studied by Ford [15]. The results, presented as surfaces of section, are shown in Fig. 2. Given the exponential nonlinearity of H , the most plausible guess as to the motion under H is that the only isolating integral is the energy. That expectation is wrong! The surfaces of section for all energies clearly show evidence of periodic behavior, and it was later shown by Henon [16] that other isolating integrals of the motion do exist, and that (13) corresponds to a completely integrable case, despite the nonlinearity. Now (14) is "much less nonlinear" than (13) and, given that (13) represents an integrable case and (14) is derived from (13), we could reasonably expect (13) also to describe an integrable system. As shown in Fig. 3, this is not the case [8]. Since (13) describes bounded motion only for $E < 1/6$ we confine attention to this energy region. For low energy ($E = 1/12$) the motion is obviously periodic, for intermediate energy, $E = 1/8$ it is mostly periodic with some nonperiodic regions, and when E approaches $1/6$ the motion is apparently nonperiodic. Therefore for, say, $E \leq 1/8$ there is an isolating integral other than the energy, but not for all $E \leq 1/6$, just the behavior described by the KAM theorem.

B. A Few Details: The Effect of Resonances (CM)

For illustrative purposes consider again a system with two degrees of freedom so that, in angle-action variables,

$$H = H_0(J_1, J_2) + V(J_1, J_2, \phi_1, \phi_2). \quad (15)$$

When $V = 0$, H_0 generates a motion for which $J_1, J_2 = \text{constants}$ and $\phi_i = \omega_i(J_1, J_2) + \phi_i^0$, $\omega_i \equiv \partial H_0 / \partial J_i$. The motion of the unperturbed system is conveniently represented on a two dimensional torus where ϕ_1, ϕ_2 are the angle

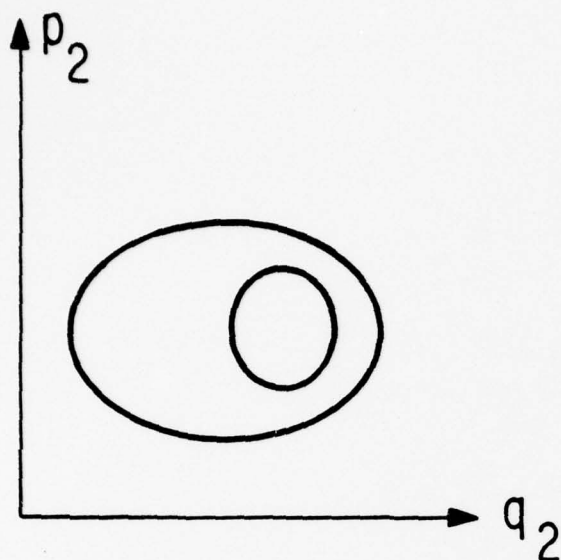


Fig. 1a Schematic representation of a Poincaré surface of section when the trajectory is quasiperiodic.

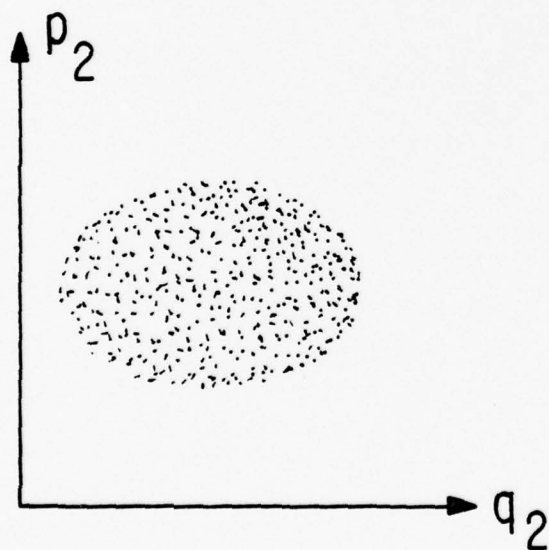


Fig. 1b Schematic representation of a Poincaré surface of section when the trajectory is not quasiperiodic.

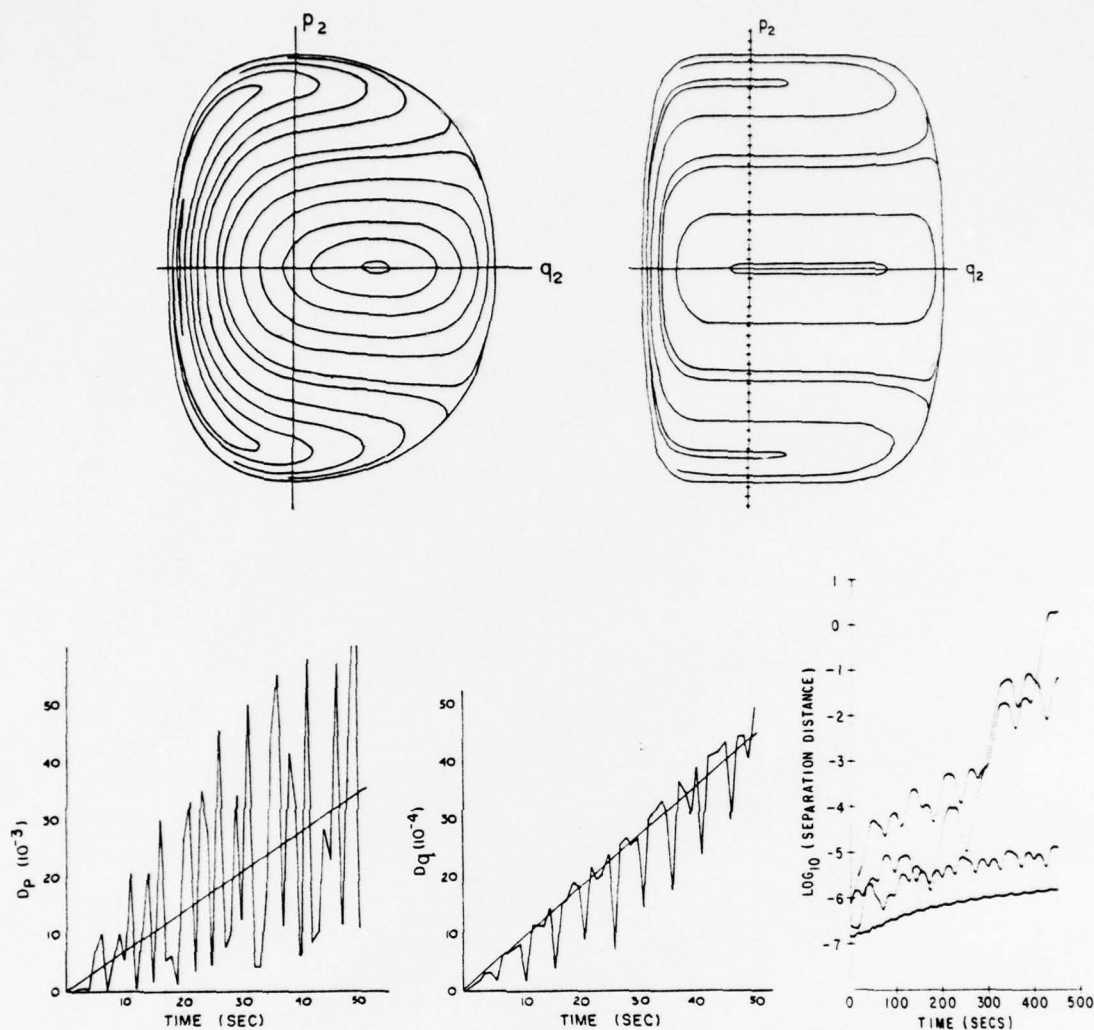


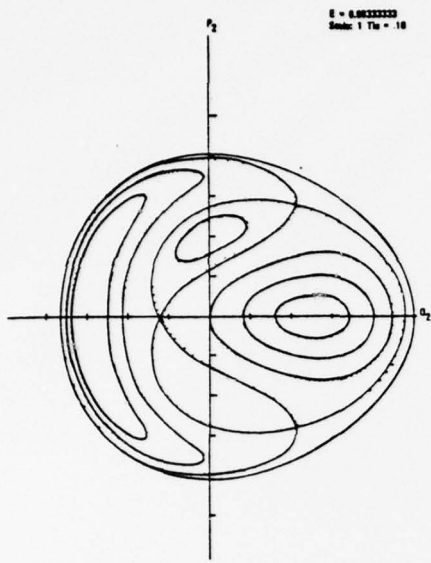
Fig. 2a Poincare surface of section for the Toda lattice. $E = 1$. From [8].

Fig. 2b Poincare surface of section for the Toda lattice. $E = 256$. From [8].

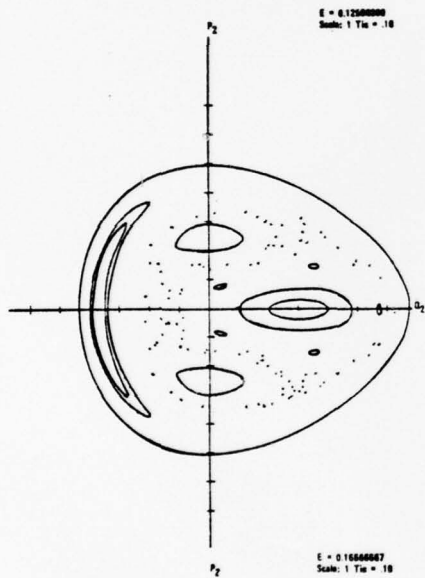
Figs. 2c, 2d The separation distances versus time in momentum and position space for two initially close trajectories of the Toda model. From [8].

Fig. 2e The separation distances versus time for two initially close trajectories of the Henon-Heiles model. $E = 1/8$. The lower curves are for trajectory pairs in the quasiperiodic region, the upper curves for trajectory pairs in the ergodic region. See Fig. 3b. From [8].

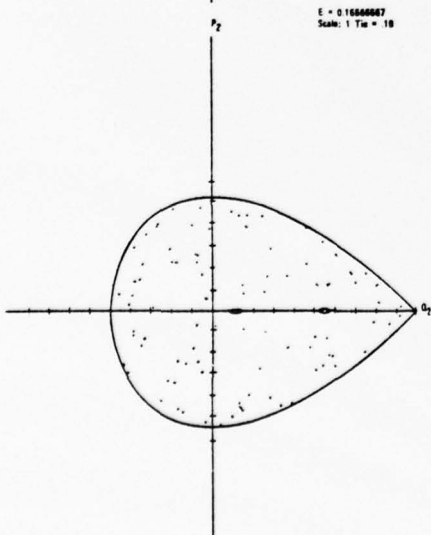
Fig. 3 Poincare surfaces of section for the Henon-Heiles model. From [8].



a. $E = 1/12$



b. $E = 1/8$



c. $E = 1/6$

coordinates and J_1, J_2 the radii. If V is small enough and the Jacobians

$$\frac{\partial(\omega_1, \omega_2)}{\partial(J_1, J_2)} \neq 0, \quad (16)$$

KAM show that the most of the unperturbed tori bearing conditionally periodic motion with incommensurate frequencies continue to exist, being only slightly perturbed by V . On the other hand, tori bearing periodic motion or very nearly periodic motion, with commensurate frequencies, or with incommensurate frequencies whose ratio is well approximated by $r/s, r, s$ small integers, are grossly deformed by V and no longer remain close to unperturbed tori. Furthermore, although the unperturbed tori with commensurate frequencies which are destroyed by $V \neq 0$ are everywhere dense, KAM show that the majority (in the sense of measure theory) of initial conditions lead to motion on preserved tori bearing conditionally periodic motion when V is sufficiently small. Thus, KAM theory shows that for small V most initial conditions lead to nonergodic motion.

What is the character of the motion not on preserved tori? Imagine H expanded in a Fourier series:

$$H = H_0(J_1, J_2) + f_{mn}(J_1, J_2) \cos(m\phi_1 + n\phi_2) + \dots \quad (17)$$

In KAM theory the angle dependent terms are eliminated by successive canonical transformations, each of which is close to the identity transformation. The final Hamiltonian is a function of transformed variables only and is "close" to the original Hamiltonian. If this can be accomplished in some general sense, one finds that the unperturbed motion, for the most part, lies on tori close to unperturbed tori.

To illustrate these ideas suppose the only important coupling term in (17) is f_{mn} (as displayed) [17]. Then to eliminate the term $\cos(m\phi_1 + n\phi_2)$ introduce the canonical transformation

$$F = \mathcal{Q}_1 \theta_1 + \mathcal{Q}_2 \theta_2 + B_{mn}(\mathcal{Q}_1, \mathcal{Q}_2) \sin(m\theta_1 + n\theta_2) \quad (18)$$

with $\mathcal{Q}, \theta$ the transformed action-angle variables, and B_{mn} to be determined. If $B_{mn} = 0$, then $\mathcal{Q}_i = J_i, \theta_i = \phi_i$. Applying F to H ,

$$H = H_0(\mathcal{Q}_1, \mathcal{Q}_2) + \{ [m\omega_1(\mathcal{Q}_1, \mathcal{Q}_2) + n\omega_2(\mathcal{Q}_1, \mathcal{Q}_2)] B_{mn} + f_{mn}(\mathcal{Q}_1, \mathcal{Q}_2) \} \cos(m\theta_1 + n\theta_2) + \dots, \quad (19a)$$

$$\omega_i(\mathcal{Q}_1, \mathcal{Q}_2) = \frac{\partial H_0}{\partial \mathcal{Q}_i}. \quad (19b)$$

To lowest order, the angle dependent term is eliminated if

$$B_{mn}(J_1, J_2) = - \frac{f_{mn}(J_1, J_2)}{m\omega_1(J_1, J_2) + n\omega_2(J_1, J_2)}, \quad (20)$$

which requires that $m\omega_1 + n\omega_2 \neq 0$ or be very small compared to f_{mn} . If the denominator is small compared to f_{mn} , B_{mn} is large, and the transformation is not close to the identity transformation, hence the transformed motion is not close to the unperturbed motion. Consequently, if there exists a band of frequencies ω_2 for which

$$|m\omega_1(J_1, J_2) + n\omega_2(J_1, J_2)| \ll |f_{mn}(J_1, J_2)|, \quad (21)$$

then the angle dependent term grossly distorts an associated zone of unperturbed tori bearing the frequencies satisfying the inequality. In general, if one Fourier component satisfies the inequality, there will be additional terms $\cos(m'\phi_1 + n'\phi_2)$ in H with ratios m'/n' sufficiently close to m/n that the inequality is also satisfied for them-- hence the zone of unperturbed tori distorted by the displayed term will simultaneously be affected by many other angle dependent terms.

Note that the inequality cited is a kind of resonance relationship which, if satisfied, asserts that $\cos(m\phi_1 + n\phi_2)$ resonantly couples the oscillators when their frequencies lie in the designated bands. When V is small, hence all f_{mn} small, such resonance zones are narrow and the KAM theorem shows that the totality of all resonant zones is small relative to the measure of the allowed phase space. We expect that as V and f_{mn} increase, or as E increases, the measure of the resonant zones will also increase until most of phase space is filled by them. KAM theory thereby predicts an amplitude instability for conservative nonlinear oscillator systems permitting a transition between predominantly quasi-periodic and ergodic motion.

In general, it is found that:

- (i) A Hamiltonian of the form

$$H = H_0(J_1, J_2) + f_{mn}(J_1, J_2) \cos(m\phi_1 + n\phi_2)$$

has an "extra" well defined constant of the motion:

$$C = nJ_1 - mJ_2.$$

- (ii) An m - n resonance for $m \neq n$ introduces a chain of m islands in the J_1 plane and a chain of n islands in the J_2 plane. (Islands are ovals surrounding points representing stable periodic orbits).
- (iii) Isolated resonances distort the unperturbed tori by introducing, in pairs, new stable and unstable periodic orbits.
- (iv) An m - n resonance zone appears abruptly, in general at some $E \geq 0$, and is bounded by a separatrix which passes through the unstable periodic solutions.
- (v) The m - n resonance zones decrease in size rapidly as m and n increase.

Several models of coupled nonlinear oscillator systems have been studied [8], [18], [19] by numerical integration of the equations of motion. A common feature of the results is the existence of isolating integrals of the motion other than the energy at low energy, and the apparent lack of such isolating integrals at high energy. Also, the transition from periodic to apparently stochastic behavior of the trajectory is smooth but abrupt as the system energy increases. The magnitude of the energy at the transition is dependent on the number of oscillators in the system. For small coupled systems, say two or three oscillators, it is about one half to two thirds of an oscillator dissociation energy. For a system with many oscillators it is, typically, larger than an oscillator dissociation energy, but only a very small fraction of the total energy of the system, and that fraction decreases as the number of oscillators increases.

Several interpretations of the dynamics underlying the KAM transition have been proposed. There is not time to discuss these, but a categorization of the ideas involved is worthwhile. One, due to Zaslavski and Chirikov [11], is based on the properties of the nonlinear resonances of the system. It is asserted that as long as there are no nonlinear resonances, the trajectory of the system is nonergodic. The KAM transition is, then, associated with the onset of overlap of nonlinear resonances of the system, which overlap leads to ergodic behavior of the trajectory. Another, I think due to Ford [8], associates the KAM transition with a dramatic increase with energy in the number of hyperbolic fixed points of the time evolution operator of the system. A third, recently published by Duff and Brumer [10], associates the KAM transition with a local instability, i.e. a region of the energy surface for which characteristic frequencies vanish. A fourth, proposed by Mo [9], is not easy to characterize. It is known that in the non-ergodic region the motion of the system is such that two trajectories, starting from nearby points, separate linearly in time, whereas in the ergodic region two such trajectories separate exponentially in time. Mo has used a projection operator scheme to generate an equation of motion for the separation between two trajectories. This formalism is truncated at an early stage to yield a manageable approximate equation of motion.

All of the proposed interpretations cited above appear to successfully predict the KAM transition in many cases, but also to fail for at least one case. Clearly, we are a long way from fully understanding the detailed nature of the dynamical state of a system near to a KAM transition.

C. Application to Model Molecular Systems (CM)

To see how the ideas mentioned in Sections IIA and IIB can be applied to molecular dynamics I shall briefly sketch an analysis by Oxtoby and Rice [20]. This analysis is intended to elucidate the relationship between nonlinear resonances and statistical behavior in intramolecular energy exchange. As throughout this section, classical mechanics is used.

The molecular model considered consists of a "critical" nonlinear oscillator driven by coupling to "other" vibrational modes; rotation-vibration interaction is neglected. Oxtoby and Rice choose bond-angle coordinates to describe the motions in the system.

When energy transfer due to interaction between non-bonded atoms is neglected

the potential energy is separable in bond-angle coordinates, and the kinetic energy is of the form [21]

$$K.E. = \frac{1}{2} \sum_{i,j} p_i G_{ij} p_j. \quad (22)$$

G_{ij} depends on the bond lengths, angles and constituent masses. Suppose G_{ij} is approximated by its value for the equilibrium configuration of the molecule, denoted G_{ij}^0 . Then the molecular Hamiltonian has the simple form

$$\begin{aligned} H &= H_0 + V \\ &= \sum_i \left[U_i(q_i) + \frac{1}{2} G_{ii}^0 p_i^2 \right] + \sum_{i < j} G_{ij}^0 p_i p_j. \end{aligned} \quad (23)$$

When G_{ij}^0 vanishes, as in the coupling of bond bending and bond stretching in a linear molecule, the next higher term in G_{ij} is retained and V is only slightly more complicated. Note that V is pairwise additive between modes. Also, for a large molecule many of the coupling terms are zero since G has matrix elements only between nearby stretching and bending modes. Furthermore the perturbation averages to zero over a vibrational period. Then the dominant effect of V will arise through near resonant coupling of two modes. Oxtoby and Rice now transform to action-angle variables. Then V becomes

$$\begin{aligned} V &= \sum_{i < j} V^{ij}(J_i, \phi_i, J_j, \phi_j) \\ 2V^{ij} &= \sum_{m,n} V_{mn}^{ij}(J_i, J_j) e^{i(m\phi_i + n\phi_j)} + C.C. \end{aligned} \quad (24)$$

A resonance occurs when

$$\frac{d}{dt}(m\phi_i + n\phi_j) = 0, \quad (25)$$

or

$$m\omega_i(J_i) + n\omega_j(J_j) = 0. \quad (26)$$

For given total energy in the two interacting modes i, j , the resonance condition defines a resonance center--denoted J_i^r, J_j^r --in phase space for each m, n . Close to the resonance center the nonresonant terms in V^{ij} can be neglected since they are small relative to resonant term. Then, near a resonance the total Hamiltonian simplifies to

$$H_r \approx \omega_i' \frac{(\Delta J_i)^2}{2} + \omega_j' \frac{(\Delta J_j)^2}{2} + V_{mn}^{ij}(J_i^r, J_j^r) \cos(m\phi_i + n\phi_j), \quad (27)$$

with

$$\begin{aligned}\Delta J_i &\equiv J_i - J_i^r, \\ \omega_i' &\equiv \left(\frac{d\omega_i}{dJ_i} \right)_{J_i = J_i^r}.\end{aligned}\quad (28)$$

By virtue of conservation of energy in the two interacting oscillators

$$\Delta J_j = \frac{\partial J_j}{\partial J_i} \Delta J_i, \quad (29)$$

hence

$$\begin{aligned}H_r = & \left[\omega_i' + \omega_j' \left(\frac{\partial J_j}{\partial J_i} \right)^2 \right] \frac{(\Delta J_i)^2}{2} \\ & + V_{mn}^{ij}(J_i^r, J_j^r) \cos(m\phi_i + n\phi_j).\end{aligned}\quad (30)$$

Note that $(\partial J_j / \partial J_i)$ is to be calculated subject to conservation of energy in the pair of oscillators i, j .

The reduced form for H_r (30) is the Hamiltonian for a simple pendulum. When ΔJ_i is small enough the restoring force in V_{mn}^{ij} will pull the resonance back toward the resonance center. The width of the resonance is determined by the range of J_i over which the "pendulum" is stable. This is

$$(\Delta J_i)_{mn} = 4 \left[|V_{mn}^{ij}| / \left| \omega_i' + \left(\frac{\partial J_j}{\partial J_i} \right)^2 \omega_j' \right| \right]^{1/2}, \quad (31)$$

and the width in energy space is

$$\begin{aligned}(\Delta E_i)_{mn} &\approx \left(\frac{\partial E_i}{\partial J_i} \right)_{J_i = J_i^r} (\Delta J_i)_{mn} \\ &= 4 \omega_i(J_i^r) \left[|V_{mn}^{ij}| / \left| \omega_i' + \left(\frac{\partial J_j}{\partial J_i} \right)^2 \omega_j' \right| \right]^{1/2}.\end{aligned}\quad (32)$$

When the energy lies within $(\Delta E_i)_{mn}/2$ of E_i^r the system will be stabilized and will oscillate around the resonance center. Since for every choice of m, n there is a resonance, the set of resonance centers is dense in action space. But, the resonance widths decrease rapidly as m, n increase so that resonance overlap considerations can be restricted to only the first few resonances.

Oxtoby and Rice propose that the molecular dynamics can be qualitatively classified according to the locations and widths of the nonlinear resonances (26). Phase space is then divided into three parts:

- (i) The representative point lies outside all resonances. Then the energies of the

different vibrational modes change slowly.

(ii) The representative point moves under the influence of a single resonance. In this case the energies in the resonantly coupled modes can, under certain conditions, change rapidly, but the motion is periodic, and the resonance is stabilized.

(iii) The representative point is simultaneously influenced by several resonances: numerical studies indicate that then the trajectories appear to behave stochastically, erratically filling the phase space.

The behavior described under (iii) leads to the contention that the stochasticity arising from overlap of nonlinear resonances [11] leads to rapid energy exchange between vibrational modes, and is the ultimate justification for RRKM theory. Oxtoby and Rice have studied this contention by examining simple models. For example, suppose that resonance between a pair of oscillators dominates the approach to stochasticity. Take

$$H_0 = \sum_i [U_i(q_i) + \frac{1}{2} G_{ii}^0 p_i^2], \quad (33)$$

$$U_i(q_i) = D_i (e^{-2q_i/a_i} - 2e^{-q_i/a_i} - 1), \quad (34)$$

where D_i is the bond dissociation energy and a_i defines the length scale for the potential. The frequency of small amplitude motion is

$$\Omega_i = (2D_i G_{ii}^0 / a_i^2)^{1/2}. \quad (35)$$

In action-angle variables H_0 is

$$H_0 = \sum_i [D_i - D_i (1 - \Omega_i J_i / 2D_i)^2], \quad (36)$$

$$\omega_i \equiv \left(\frac{\partial H}{\partial J_i} \right) = \Omega_i (1 - \Omega_i J_i / 2D_i). \quad (37)$$

Since

$$E_i = D_i - D_i (1 - \Omega_i J_i / 2D_i)^2, \quad (38)$$

one can write

$$\omega_i(E_i) = \Omega_i (1 - E_i / D_i)^{1/2}. \quad (39)$$

The corresponding momentum is

$$p_i = \left(\frac{2D_i}{G_{ii}^0} \right)^{1/2} \frac{\omega_i}{\Omega_i} \left(1 - \frac{\omega_i^2}{\Omega_i^2} \right) \frac{\cos \phi_i}{1 + (1 - \omega_i^2 / \Omega_i^2)^{1/2} \sin \phi_i}, \quad (40)$$

where $\phi_i \equiv \omega_i t + \theta_i$ is the angle variable of the canonical transformation. Continuing, (32) becomes,

$$\begin{aligned}
 (\Delta E_i)_{mn} = & 8\sqrt{2} \left[\frac{D_i D_j (G_{ij}^0)^2}{\Omega_i^2 \Omega_j^2 G_{ii}^0 G_{jj}^0} \right]^{1/4} \left[\frac{\omega_i^3 \omega_j^3}{\frac{\Omega_i^2 \omega_j^2}{D_i} + \frac{\Omega_j^2 \omega_i^2}{D_i}} \right] \\
 & \times \left[\frac{1 - \omega_i / \Omega_i}{1 + \omega_i / \Omega_i} \right]^{m/4} \left[\frac{1 - \omega_j / \Omega_j}{1 + \omega_j / \Omega_j} \right]^{n/4},
 \end{aligned}
 \tag{41}$$

and

$$m\omega_i(E_i) = n\omega_j(E_j). \tag{42}$$

The results of numerical calculations for this model reveal the following:

- (i) In typical two oscillator resonance dominated dynamics there will be significant non-random behavior over the entire energy range up to D_i . Slow energy redistribution occurs because the system can be "trapped" for many vibrational periods near the centers of isolated nonlinear resonances. (See Figs. 4 and 5).
- (ii) As the total energy increases the relative volume of phase space occupied by overlapping resonances increases, so that energy redistribution becomes the behavioral norm. (See Figs. 4, 5 and 6).
- (iii) If one bond dissociation energy becomes large, the corresponding oscillator becomes more harmonic, leading to a decrease in the width and (especially) number of nonlinear resonances.
- (iv) As the two frequencies Ω_i, Ω_j move apart, the number of nonlinear resonances decreases, especially so at low energy.
- (v) Resonance widths are proportional to

$$\left[(G_{ij}^0)^2 / G_{ii}^0 G_{jj}^0 \right]^{1/4}$$

so that large changes in masses and bond angles are necessary to affect the resonances and their overlap.

- (vi) Harmonic bending modes (especially low frequency modes) are strongly coupled to the critical bond stretch only when the critical mode is very close to dissociation. Then, a likely pathway for energy transfer to a breaking bond involves, first, transfer from other bond stretching modes and, second, only when the critical bond is close to dissociation, transfer from the bending modes. (See Fig. 6).

What happens when there are many nonlinear oscillators? For two interacting oscillators the zeroth order energy surface is one dimensional. In this case there is only one path from a given point to any other, hence narrow resonances do not overlap. For $n > 2$ oscillators, the energy surface is of dimension $n - 1$, and centers of resonances are not points, but rather $n - 2$ dimensional surfaces.

- (vii) Many oscillator case: Suppose one oscillator is singled out for attention. If a large amount of energy is put into this oscillator relaxation will proceed in two stages. First there will occur transfer of energy to a few modes directly coupled to the critical oscillator and, second, transfer from these modes to the rest of the molecule. We expect the second process to be, basically, "statistical" in character. The same argument applies to the reverse process, namely energizing some vibrational mode. The analysis

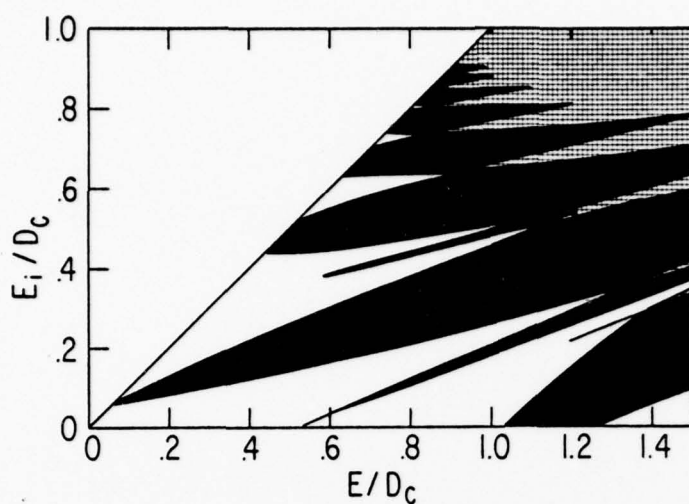


Fig. 4 Resonance structure for CC stretch (1000 cm^{-1}) coupled to CH stretch (2900 cm^{-1}); CH dissociation energy is $2D$, where D is the CC dissociation energy. Black areas indicate single resonances; cross-hatched areas indicate resonance overlap. E is the total energy in the two oscillators, E_i the energy in the critical CC stretching mode.

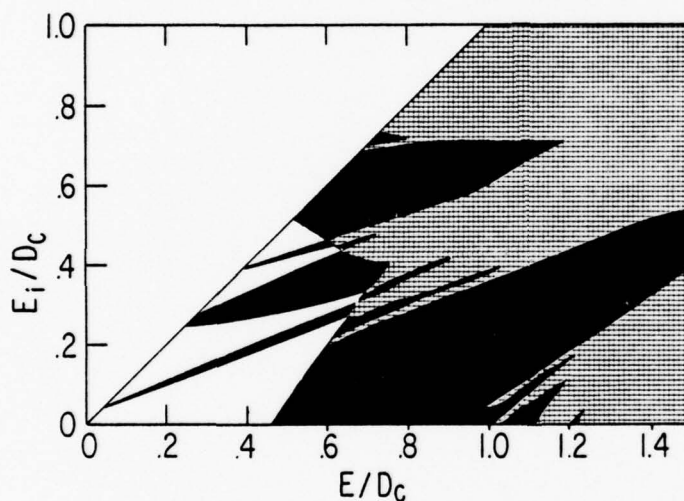


Fig. 5 Resonance structure for CC stretch (1000 cm^{-1}) coupled to another CC stretch (1300 cm^{-1}); the second CC dissociation energy is $1.5 D$.

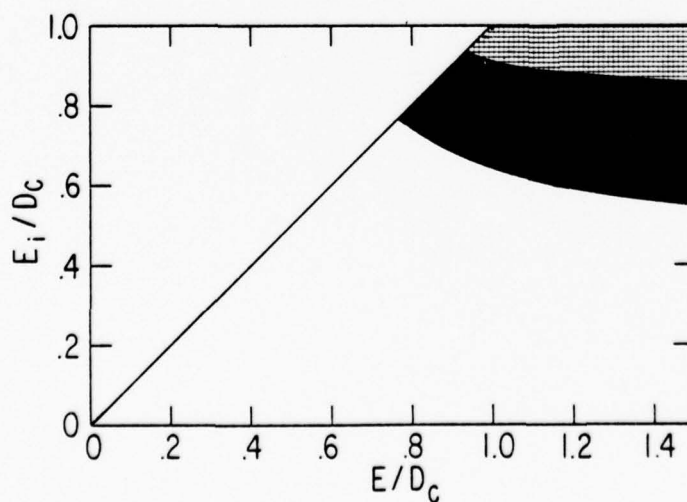


Fig. 6 Resonance structure for CC stretch (1000 cm^{-1}) coupled to CCH bend (400 cm^{-1}); the bending mode is taken to be harmonic.

of the first process leads to consideration of an ensemble of one-dimensional resonance distributions, each member of the ensemble corresponding to a different distribution of non-critical energy amongst the $n-1$ oscillators directly coupled to the critical oscillator. The general conclusions concerning stochasticity in the two oscillator case are found to remain valid in the many oscillator case. (See Fig. 7). It is found that as the number of oscillators increases, the energy of each one (on average) decreases. Consequently, the noncritical oscillators are closer to harmonic and each one has fewer and narrower resonances with the critical oscillator. Thus resonance overlap need not increase with the number of oscillators directly coupled to the critical oscillator. (See Fig. 7).

A direct confirmation of the Oxtoby-Rice analysis can be obtained by comparison with studies of dissociating trajectories on an energy surface. Identifying the onset of stochasticity with overlap of nonlinear resonances is in agreement with Bunker's molecular dynamics studies of linear triatomic molecules and the existence of a random distribution of lifetimes against fragmentation. (See Fig. 8).

It is important to remark that the rapidity of mode to mode energy transfer depends on the nature of the modes used to describe the dynamics of the system. In particular, the small vibrational amplitude, normal mode, description so useful in spectroscopic analysis breaks down for large amplitude motion. In the preceding paragraphs it was argued that if bond stretching and bond bending coordinates are adopted there can be localization of an initial excitation up to an appreciable fraction of a bond dissociation energy. Parr and Kupperman [22] have examined energy exchange between normal modes in an anharmonic triatomic molecule. That is, taking the bond stretching to be defined by a Morse potential, the same linear combinations that define small amplitude normal modes in terms of bond stretches were used for large amplitude motion. Note that this model includes diagonal anharmonicity within bonds, but no bond-bond interaction. For a symmetric triatomic, M_3 with half the energy of dissociation in the asymmetric stretch, half that energy is exchanged with the other (defined) normal modes in less than one period of vibration. As shown in Fig. 9, there does not appear to be any regularity in the pattern of mode to mode energy exchange. A similar model of $CFNO$ [22] with half its dissociation energy in the symmetric stretching mode, shows evidence of nonlinear resonance trapping of energy. (See Fig. 10)

D. Large Amplitude Motion - Solitary Waves [23], [24]

There is yet another consequence of the existence of anharmonic potential energy terms in the Hamiltonian of a coupled oscillator system. Consider the fact that these anharmonicities correspond to nonlinearities in the equations of motion of the system. Now in the case of continuum wave motion corresponding nonlinearities are known to yield localizing phenomena such as shock waves. Possibly, then, nonlinearities in the oscillator dynamics could, in some circumstances, counter the tendency for energy redistribution into all available bond vibrations. An example of this behavior is provided by the Toda lattice [13] already mentioned. This model has the advantage over others that also support so called solitary waves [24] of being discrete, hence somewhat closer to molecular systems than are continuum models.

Consider an infinite one-dimensional lattice of particles of equal mass which

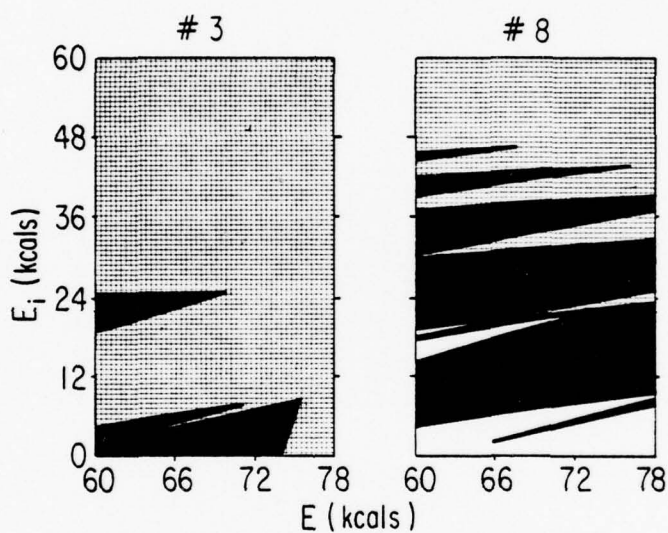
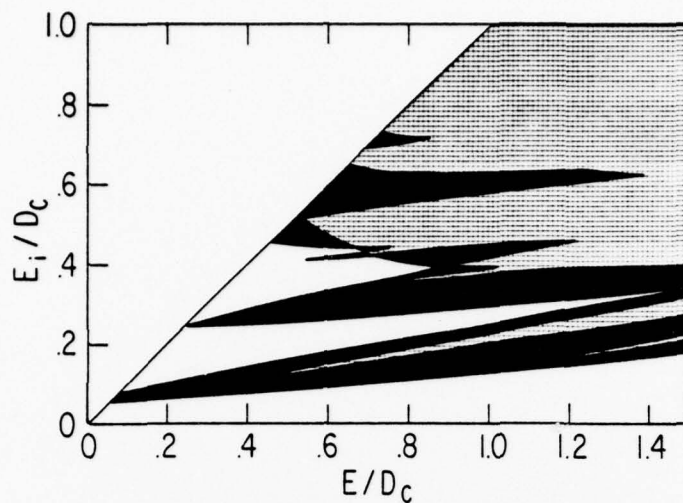


Fig. 7 Resonance structure for CC stretch (1000 cm^{-1}) coupled equally to the three modes of Figs. 4, 5 and 6. E is the total energy in all four modes, E_i the energy in the critical CC stretching mode.

Fig. 8 Resonance structures for Bunker's model #3 (a random lifetime distribution case) and #8 (a nonrandom case). Critical oscillator dissociation energies in both cases are 60 kcal. Bunker investigated the energy range from 62.5 - 75 kcal.

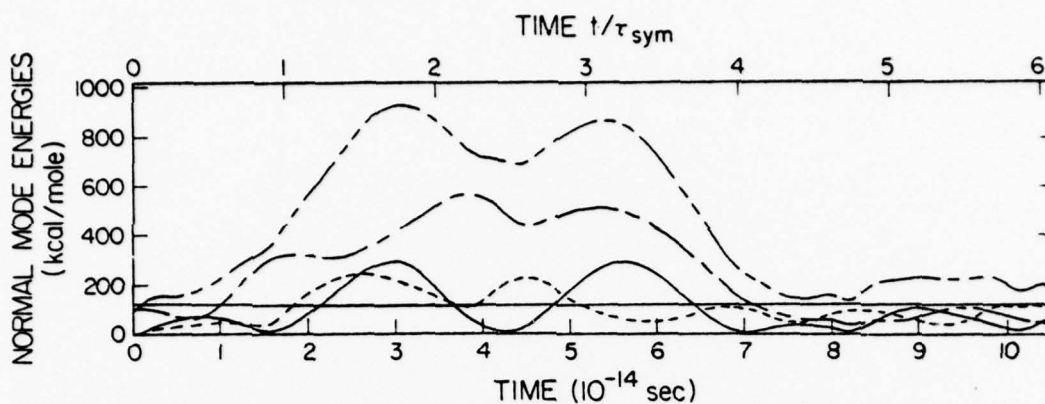


Fig. 9 Normal mode energies of anharmonic M_3 with the initial condition that the energy in the asymmetric stretch is 0.5 D. — symmetric stretch, ---- bend, — · — asymmetric stretch, — — — sum of normal mode energies. From [22].

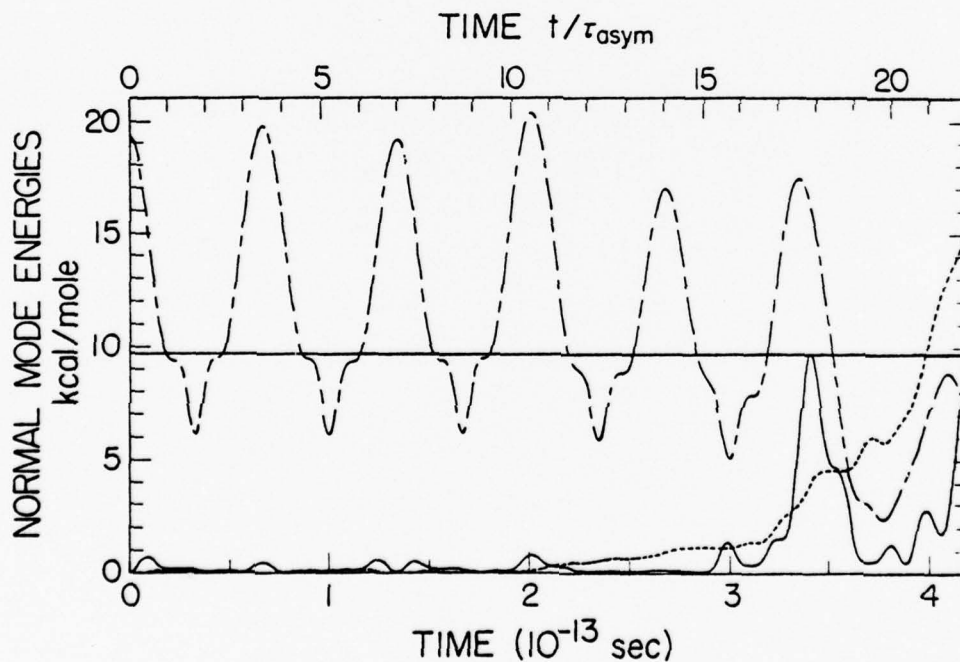


Fig. 10 Normal mode energies of anharmonic Cl NO with the initial condition that the energy in the symmetric stretch is 0.5 D. — asymmetric stretch, ---- bend, — · — symmetric stretch. From [22].

interact only with their nearest neighbors through a (Toda) potential of the form

$$V(x) = kb^2 \left[e^{-x/b} + \frac{x}{b} - 1 \right], \quad (43)$$

where x is the displacement of the bond from its equilibrium (43) length, and k and b are parameters. Note that as $b \rightarrow \infty$, the potential becomes harmonic with force constant k , and as $b \rightarrow 0$ the potential is equivalent to that between colliding hard spheres. The classical Hamiltonian for this system is

$$H = \sum_n \frac{m}{2} \dot{x}_n^2 + V(x_n - x_{n-1}), \quad (44)$$

and the equation of motion is

$$m \ddot{x}_n = kb \left[e^{-(x_{n+1} - x_n)/b} - e^{-(x_n - x_{n-1})/b} \right]. \quad (45)$$

Substitution of the new coordinates and time,

$$\begin{aligned} Q_n &= e^{-(x_n - x_{n-1})/b} - 1, \\ T &= (k/m)^{1/2} t, \end{aligned} \quad (46)$$

yields an equation of motion of the form,

$$\frac{\partial^2}{\partial T^2} \ln(1 + Q_n) = 2Q_n - Q_{n+1} - Q_{n-1}. \quad (47)$$

This equation has nondivergent solutions of two types: (1) solitary waves (single and multiple) which asymptotically may be written as linear combinations of noninteracting single solitary waves of the form [13]

$$Q_n = \sinh^2 K \operatorname{sech}^2(Kn \pm t \sinh K + \delta), \quad (48)$$

and (2) c-noidal waves. [13] The c-noidal waves may be represented as an infinite number of equally spaced solitary waves which mutually interact; their dispersion relation is different from that of the solitary waves. This is, of course, a loose classification for both types of solutions may occur simultaneously and the motion can be difficult to interpret.

For our present purposes, the behavior of both types of solutions in the harmonic and hard-core limits are particularly illustrative. In the harmonic limit the amplitude of the solitary waves approach zero and the c-noidal waves approach the normal modes of the infinite harmonic lattice. In the hard-core limit the amplitude of the c-noidal waves approach zero and the solitary waves become sharper and sharper. The analogy between this behavior and the vibrational processes which occur in molecules is too appealing to overlook. Large amplitude vibrations probe parts of the molecule's potential energy surface which are possibly better characterized by the interaction between colliding spheres

with short ranged interactions than by atoms joined by springs. It is important to note that the properties of these local excitations cannot be treated in perturbation theory beginning in the harmonic limit since the differences in the forms of the solitary wave and c-noidal excitations are equivalent to a phase transition and it is not possible to use perturbation theory to predict properties across a phase transition.

Some characteristics of solitary waves are worth noting [24]:

- (i) Solitary waves propagate for an indefinitely long time, hence a system in which such a wave is excited will be nonergodic in the absence of external disturbances.
- (ii) Solitary waves are, in most cases, stable under collision with other solitary waves (when this is so they are called solitons).
- (iii) The existence of solitary wave solutions does not, in my opinion, violate the KAM theorem since the initial conditions are rather special, hence probably excluded in the sense of measure theory from those for which the KAM topological analysis holds.
- (iv) The soliton solutions for the Toda lattice are compressional waves. There are not any dilational solitary wave solutions for the Toda lattice. This fact is of importance with respect to how boundary conditions influence the stability of solitary waves. For example, at a free end a compressional solitary wave is reflected as a dilational wave, which will not be stable. In some cases, for example the continuum analogue of the Fermi-Pasta-Ulam lattice, [25], both compressional and dilational solitary waves exist. Although it is not certain, it appears likely that lattices with harmonic and odd power anharmonic potential energy terms support only compressional solitary waves, while lattices with harmonic and even power anharmonic potential energy terms support both compressional and dilatational solitary waves.
- (v) In all cases for which the existence of solitary waves has been established rigorously, the system has an integrable equation of motion. This is a crucial point since virtually all systems of physical interest have nonintegrable equations of motion. Zabusky [26] has discussed nonintegrable systems which support solitary waves, but little is known of such systems.

What, if any, is the connection between solitary wave phenomena and molecular dynamics? I do not know the answer to that question, but I can offer the following tantalizing facts. First, the existence of solitary waves appears to be more general than might be expected from the statements of the last paragraph. Rolfe, Rice and Dancz [27] have shown, by numerical integration of the equations of motion, that large amplitude motion on a one dimensional lattice of particles interacting with a Morse potential or with a Lennard-Jones potential is described by solitary wave motion (see Figs. 11 and 12). Second, Dancz and Rice [28] have shown that the introduction of quantum mechanics to describe the atomic motion does not fundamentally alter the situation--solitary waves still describe the large amplitude motion of the one dimensional lattice. Third, evidence is emerging which suggests that solitary waves can exist in three dimensional systems [24]. Fourth, and on the other side of the coin, it is not known if solitary waves can exist on a lattice with a distribution of force constants and masses. The preliminary evidence available suggests that introduction into a one dimensional lattice of a different mass leads to destruction of a solitary wave by scattering, [29], although presumably a regular sub-lattice of particles with different mass will not have such an effect. Finally, it is not known what conditions will uniquely excite a solitary wave in a molecular system, assuming such exist.

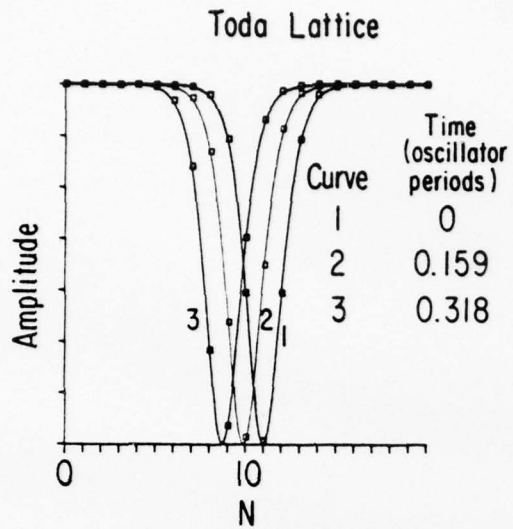
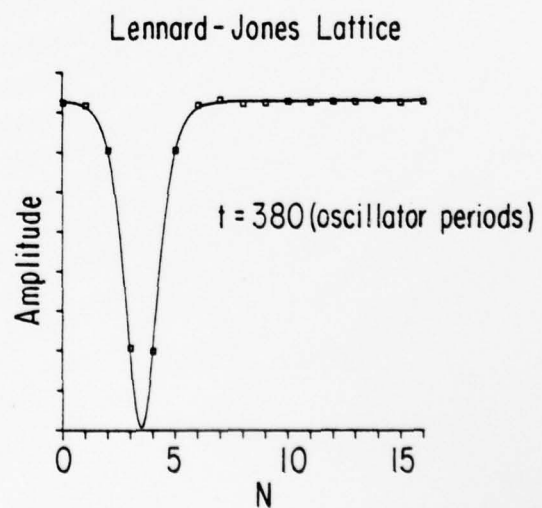
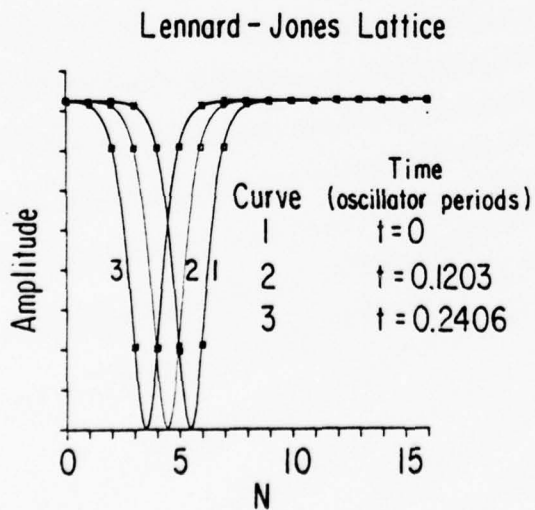
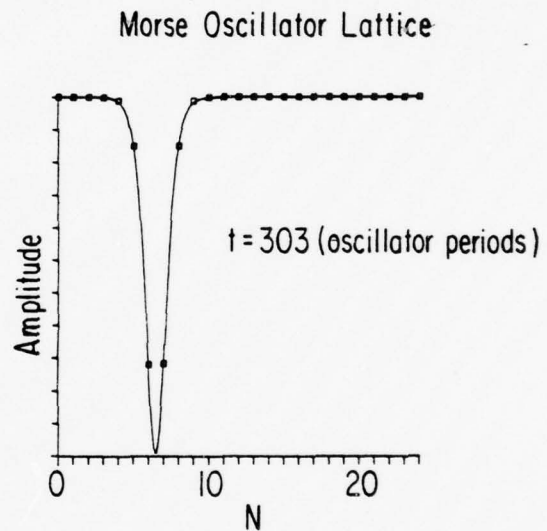
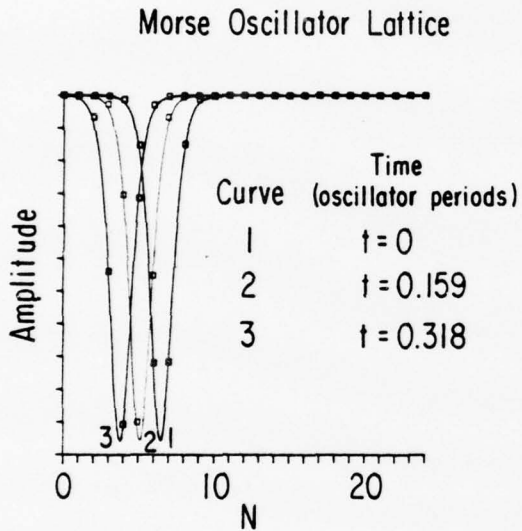


Fig. 11a Solitary wave on a Toda lattice,
11b Solitary wave on a Morse lattice.

Fig. 12 Solitary wave on a Lennard-Jones lattice.



III. Energy Transfer in Quantized Systems

In the last section it was shown that, for a system described by classical mechanics, in the absence of low order resonances among a set of coupled oscillators most trajectories are stable and quasiperiodic for small enough energy. For a system of two, three, ... oscillators the KAM transition between quasiperiodic and apparently stochastic behavior is of the order of one half to two thirds a bond dissociation energy. The relevance of this observation to the behavior of molecules depends on whether or not there are resemblances between the dynamics of classical and quantum mechanical systems.

The determination of the eigenstates of a coupled system of nonlinear oscillators has been attacked from several points of view. Major contributions have been made by Percival [30], Berry [31], Miller [32] and Marcus [33] who have advanced the semiclassical theory of bound states. These investigators have adopted the Einstein [34] generalization of the Bohr-Sommerfeld-Wilson quantization condition, namely

$$J = \frac{1}{2\pi} \oint \sum_{k=1}^N p_k dq_k = n\hbar, \quad (49)$$

where the integral over the invariant differential sum $\sum p_k dq_k$ is along closed curves in coordinate space that need not be classical trajectories. The usual Bohr-Sommerfeld-Wilson condition is defined for each separable coordinate q_k , and the corresponding action integral is taken around one cycle of the motion of the coordinate q_k . This condition depends on the choice of coordinates whereas Einstein's condition, which defines an integration over all N action functions, does not depend on the choice of coordinates. It is readily seen that the Einstein condition can be applied to motion in the region where the trajectory is quasiperiodic, but not above the KAM transition, since in that domain p_k cannot be expressed as a function of the q_k . This has led Percival [30] to classify the spectrum of a system into the categories regular and irregular, the former pertaining to the domain below the KAM transition where the trajectory is quasiperiodic, and the latter to the domain of apparent stochastic behavior of the trajectory.

Nordholm and Rice [25] have taken a different approach. In principle the eigenvalues of an arbitrarily complicated Hamiltonian can be computed by use of expansion in a complete set of basis functions and evaluation of matrix elements, though an actual calculation may be very tedious. Noting this, the important question is how an initially localized excitation spreads over the energy surface of the system. Nordholm and Rice propose to classify a state of the system as ergodic if an excitation initially not uniformly distributed over the energy surface becomes uniformly distributed as $t \rightarrow \infty$. This suggestion is deliberately constructed to be in direct correspondence with the usual definition of ergodicity on a classical energy surface. It has the advantage of being easily tested for any given set of basis states. It has the disadvantage that the conclusion of a test for this kind of ergodicity is, in general, basis dependent. Of course, a basis dependence can be connected to reality if there exists an excitation mechanism that prepares the system in one or more of the basis states.

Nordholm and Rice [35] have studied several model systems of coupled nonlinear oscillators. The Hamiltonians examined include examples with algebraic nonlinearities and with exponential (Morse function) nonlinearities, and examples with degenerate

and with nondegenerate oscillators. The basis states of the representation are, for each Hamiltonian, chosen to be the states of the corresponding decoupled set of harmonic oscillators. The calculations lead to the following conclusions:

- (i) There is nonergodic behavior, in general, below a critical energy (possibly a critical energy region). The nonergodicity is more marked and persistent for nondegenerate systems than for equivalent degenerate systems.
- (ii) For degenerate systems there are occasional global states interspersed in the local states. (A global state is one with amplitude uniformly distributed over the energy surface).
- (iii) For low energy, typically less than half the dissociation energy D , the asymptotic distribution of amplitude over the equienergetic basis states is not very sensitive to the coupling.
- (iv) Initial states with comparable excitation in all oscillators tend to evolve to global states, whereas extremal initial states with excitation mostly localized in one oscillator tend to evolve to local states.
- (v) For high energy, typically above half the dissociation energy, the asymptotic distribution of amplitude over the basis states is very sensitive to the coupling. In this case the final states achieved tend to have mixed character (e.g. a wide but uneven spread of overlaps).
- (vi) From a very crude analysis of the time evolution of the model systems it is estimated that in these cases it takes of the order of one to ten vibrational periods for an initially localized nonstationary state to achieve its asymptotic form.

Clearly, the quantum dynamics of coupled oscillator systems is analogous to the classical dynamics of these systems. In particular, a KAM transition exists. Note also how conclusion (iv) is very like the prediction that if energy is initially localized in one oscillator it requires a higher total energy to reach the region of overlap of nonlinear resonances than if the same initial energy is spread over several oscillators (see Figs. 4 - 7).

A connection between conclusions (iii) and (v) of Nordholm and Rice and Percival's notion of regular and irregular spectra has been made in a calculation by Pomphrey [36]. He studied the sensitivity of the parameterized Henon-Heiles Hamiltonian ($m=1$)

$$H = \frac{1}{2}(p_1^2 + p_2^2) + \frac{1}{2}(q_1^2 + q_2^2) + \alpha(q_1^2 q_2 - \frac{1}{3} q_2^3) \quad (50)$$

to the value of α . In this case the dissociation energy is $1/6\alpha^2$. Pomphrey computed the eigenvalues of (50) for the range $0.090 \leq \alpha \leq 0.086$ and examined the sensitivity of the spectrum as a function of the energy. This sensitivity is measured by the second difference

$$\Delta_i \equiv |\{E_i(\alpha + \Delta\alpha) - E_i(\alpha)\} - \{E_i(\alpha) - E_i(\alpha - \Delta\alpha)\}|. \quad (51)$$

Perturbation theory yields the result

$$\Delta_i \sim O(\Delta\alpha^3). \quad (52)$$

The calculations show that for $E \leq 16 = 0.74 D$ all second differences are very small. This is the regular region of the spectrum, corresponding to localized asymptotic

distribution over the basis states, and to quasiperiodic motion in the classical limit. For $E > 16$ eigenvalues are found with corresponding Δ_i orders of magnitude larger, i.e. the spectrum is very sensitive to small changes in α . This is the irregular region of the spectrum, corresponding to global asymptotic distribution over the basis states, and to apparently stochastic motion in the classical limit (see Fig. 13). It is also illuminating to compare the coverage of the surface of section by the apparently stochastic trajectory with the region of Hilbert space wherein the spectrum is very sensitive to the coupling. For the classical Henon-Heiles Hamiltonian the total area covered by unstable trajectories up to energy E is

$$I(E) = \int \alpha_I(E) dE$$

$$\alpha_I(E) = 0, E < 0.68D; \alpha_I(E) = 3.125\left(\frac{E}{D}\right) - 2.125, E > 0.68D, \quad (53)$$

where "total area" means the relative area of the surface of section. The quantity is to be compared with

$$S(E) = \frac{1}{D} \sum_i^E n_I(E_i) \langle \Delta E_i \rangle, \quad (54)$$

corresponding to the part of Hilbert space where the spectrum is very sensitive to a change in α . Here $n_I(E) = 1$ if E_i is very sensitive to the value of α , $n_I(E_i) = 0$ otherwise. Also,

$$\langle \Delta E_i \rangle = \frac{1}{2} (E_{i+1} - E_{i-1}). \quad (55)$$

As shown in Fig. 14 the quantum mechanical results follow, qualitatively, the shape of the classical curve. ($I(E)$ and $S(E)$ have different dimensionality, hence cannot agree quantitatively.)

IV. Ergodicity and Reaction Rate -- Model Considerations

Except for the comparison of the Oxtoby-Rice predictions with the distribution of fragmentation lifetimes determined in Bunker's trajectory calculations. I have thus far confined the discussion to the behavior of the bound states of a system of coupled nonlinear oscillators. I now wish to consider the influence, or lack of influence, of the nature of intramolecular energy exchange on the rate of a fragmentation reaction. At first sight it appears that, because the KAM transition typically occurs for $E < D$, the rate of fragmentation should be accurately accounted for by a statistical model. A deeper examination reveals that the matter is not so simple. First, the very nature of the irregular spectrum suggests that a decomposition rate might not be a monotone function of the energy. Second, resonances in the localized states of the bond that breaks could conceivably be derived from nonergodic states of the molecule interspersed sparsely in the ergodic region of states. Third, the matrix elements coupling different vibrations of the molecule might vary over such a large range that only a subset of all vibrations is effectively coupled on the time scale of the reaction.

To determine if any of these possibilities is important Nordholm and Rice [37] developed an exact formal theory of the fragmentation reaction, and made calculations for an approximate model. Consider an initial bound state $|\psi\rangle_0$, with time development

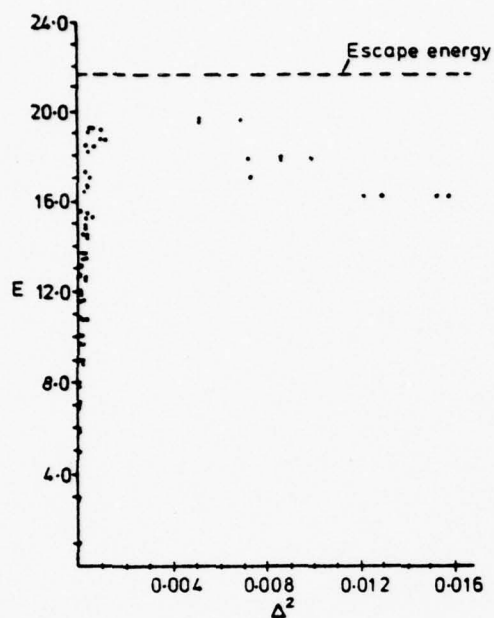


Fig. 13 Sensitivity of the eigenvalues of the Henon-Heiles model Hamiltonian to small changes in coupling. From [30].

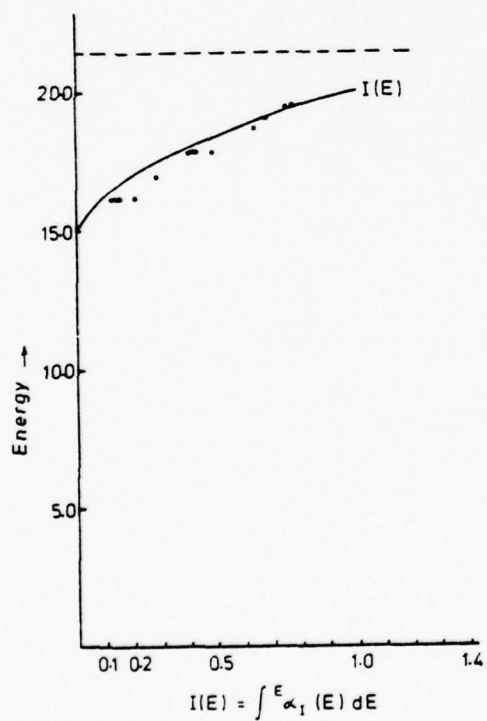


Fig. 14 Comparison of area of surface of section covered by non-periodic trajectory, and domain of Hilbert space where the eigenvalues are sensitive to small changes in coupling. From [30].

$$\frac{\partial}{\partial t} |\psi\rangle_t = -\frac{i}{\hbar} \hat{H} |\psi\rangle_t. \quad (56)$$

Let $\mathcal{X}$ be the complete Hilbert space corresponding to $\hat{H}$. The space $\mathcal{X}$ contains both bound and continuum states. Define a projection operator $\hat{P}_B$ such that

$$\hat{P}_B \mathcal{X} = \mathcal{B}, \quad (57)$$

where $\mathcal{B}$ is the domain of Hilbert space corresponding to bound levels. Then

$$W_B(t) = \langle \psi | \hat{P}_B | \psi \rangle_t = \| \hat{P}_B |\psi\rangle_t \|^2 \quad (58)$$

is the probability of finding the molecule in a bound level. We seek the equation of motion of $\hat{P}_B |\psi\rangle_t$. Define $\hat{P}_F \equiv 1 - \hat{P}_B$. Then

$$\begin{aligned} \frac{\partial}{\partial t} \hat{P}_B |\psi\rangle_t &= -\frac{i}{\hbar} \hat{H}_{BB} \hat{P}_B |\psi\rangle_t - \frac{i}{\hbar} \hat{H}_{BF} \hat{P}_F |\psi\rangle_t, \\ \frac{\partial}{\partial t} \hat{P}_F |\psi\rangle_t &= -\frac{i}{\hbar} \hat{H}_{FF} \hat{P}_F |\psi\rangle_t - \frac{i}{\hbar} \hat{H}_{FB} \hat{P}_B |\psi\rangle_t, \end{aligned} \quad (59)$$

$$\begin{aligned} \hat{H}_{BB} &\equiv \hat{P}_B \hat{H} \hat{P}_B, & \hat{H}_{BF} &\equiv \hat{P}_B \hat{H} \hat{P}_F, \\ \hat{H}_{FF} &\equiv \hat{P}_F \hat{H} \hat{P}_F, & \hat{H}_{FB} &\equiv \hat{P}_F \hat{H} \hat{P}_B. \end{aligned} \quad (60)$$

Suppose the molecule starts in the bound region, so that $\hat{P}_F |\psi\rangle_0 = 0$. Then

$$\hat{P}_F |\psi\rangle_t = -\int_0^t ds e^{-is\hat{H}_{FF}/\hbar} \left(\frac{i}{\hbar}\right) \hat{H}_{FB} \hat{P}_B |\psi\rangle_{t-s} \quad (61)$$

and

$$\begin{aligned} \frac{\partial}{\partial t} \hat{P}_B |\psi\rangle_t &= -\frac{i}{\hbar} \hat{H}_{BB} \hat{P}_B |\psi\rangle_t \\ &\quad - \frac{1}{\hbar^2} \int_0^t ds \hat{H}_{BF} e^{-is\hat{H}_{FF}/\hbar} \hat{H}_{FB} \hat{P}_B |\psi\rangle_{t-s}. \end{aligned} \quad (62)$$

Eq. (62) is easily interpreted: $\hat{H}_{FB} \hat{P}_B |\psi\rangle_{t-s}$ measures the flow of amplitude from $\mathcal{B}$ to $\mathcal{F}$ at $t-s$. Then $\exp(-i\hat{H}_{FF}s/\hbar)$ propagates this amplitude within $\mathcal{F}$ forward in time from $t-s \rightarrow t$, and $\hat{H}_{BF}$ measures how much of it is returned to $\mathcal{B}$ at t . The integration sums these effects from $t=0$. The term

$$-\frac{1}{\hbar^2} \int_0^t ds \hat{H}_{BF} e^{-is\hat{H}_{FF}/\hbar} \hat{H}_{FB} \hat{P}_B |\psi\rangle_{t-s}$$

leads to a decrease in the norm of $\hat{P}_B |\psi\rangle_t$, hence to dissipation, because the flow out of B will exceed the flow in given that amplitude is propagated away from the boundary of B by the action of $\exp(-i\hat{H}_{FF}S/\hbar)$, diminishing the net flow back into B . Note that when $\hat{H}_{BF}$ is set equal to zero the formalism describes exactly the relaxation in the manifold of bound levels.

The advantage offered by the Nordholm-Rice analysis is that at the formal level the equations of motion of $\hat{P}_B |\psi\rangle_t$ and $\hat{P}_F |\psi\rangle_t$ have been decoupled. The price paid for this decoupling is that the equation of motion of $\hat{P}_B |\psi\rangle_t$ depends on the "memory" of the motion. Nevertheless there is a net gain in that the structure of the formalism suggests approximations to the N-body dynamics different from those suggested by other formalisms, especially when the analogy with the statistical mechanics of irreversibility is exploited.

A "simplest model" based on this formalism is generated as follows. Set

$$\hat{H}_{BF} e^{-iS\hat{H}_{FF}/\hbar} \hat{H}_{FB} \rightarrow \hat{H}_{BF} \hat{C}_{FF} \hat{H}_{FB} \delta(S), \quad (63)$$

where $\hat{C}_{FF}$ is an operator that measures the lifetime of the amplitude in a transition region in F , close to the boundary of B . In this transition region $\hat{H}_{BF} \neq 0$. Then

$$\frac{\partial}{\partial t} \hat{P}_B |\psi\rangle_t = -\frac{i}{\hbar} \hat{H}_{BB} \hat{P}_B |\psi\rangle_t - \frac{1}{\hbar^2} \hat{H}_{BF} \hat{C}_{FF} \hat{H}_{FB} \hat{P}_B |\psi\rangle_t, \quad (64)$$

and in this (Markoffian) approximation the projected bound state amplitude changes in time according to the effective Hamiltonian

$$\hat{H}_{eff} = \hat{H}_{BB} - i\hat{H}_D = \hat{H}_{BB} - \frac{i}{\hbar} \hat{H}_{BF} \hat{C}_{FF} \hat{H}_{FB}, \quad (65)$$

which has the dissipative component $-i\hat{H}_D$. This form will be valid if:

- (i) the time spent in the transition region T where $\hat{H}_{BF} \neq 0$ is very short on the time scale of the dynamics in B ,
- (ii) escape from T into $F-T$ is irreversible.

Condition (i) requires T to be small relative to B ; condition (ii) requires that

$$\hat{H}_{BF} e^{-i\hat{H}_{FF}S/\hbar} \hat{H}_{FB} \rightarrow 0$$

rapidly. Note that if the forces between separating fragments have short range a spatial boundary can be used to define B and T -- the approach is then reminiscent of the R -matrix approach to scattering [38]. However, other separations defining B and T can be used as desired and as convenient. The Markoffian $\hat{H}_{eff}$ has the same character as phenomenologically postulated in the optical potential method applied to the decay of atomic or molecular states [39]. As to the properties of $\hat{H}_{eff}$ defined by (65), the most important for our purposes are the following:

- (iii) For a reasonable separation of $\mathcal{X}$, $\hat{H}_{BF}$ (and $\hat{H}_D$) will vanish except in small region T_B . An initial state localized to $B-T_B$ can only dissociate if

$e^{-i\hat{H}_{BS}t/\hbar}$ propagates the initial amplitude to T_B . If the eigenstates of $\hat{H}_{BS}$ are ergodic such propagation will always take place; in contrast, nonergodic states completely localized to $B-T_B$ lead to only partial dissociation or none at all.

(iv) $\hat{H}_{eff}$ is not a Hermitian operator, and in general is not a normal operator, hence $\hat{H}_{eff}\hat{H}_{eff}^\dagger$ does not commute with its adjoint ($\hat{H}_{BS}$ does not commute with $\hat{H}_D$). Consequently $\hat{H}_{eff}$ need not have a complete set of orthonormal eigenstates. However, for each root of the characteristic equation there is at least one linearly independent eigenstate and no more than n (the multiplicity of the root). If all the roots of the characteristic equation are nondegenerate the operator will have a complete set of linearly independent eigenstates-- such operators are called semi-simple. We assume that $\hat{H}_{eff}$ is semisimple.

(v) The eigenvalues of $\hat{H}_{eff}$ will, in general, be complex; the eigenstates will be complete but not orthogonal.

To actually compute the properties of a particular model, an initial state is expanded in the basis of the eigenstates $\{|E\rangle\}$ of $\hat{H}_{eff}$, with $E = E_R + iE_I$. When the initial state is a superposition of the $\{|E\rangle\}$ the decay will be, in general, not a pure exponential form. If $\hat{H}_{eff}$ were normal (so the eigenstates are orthonormal) the decay would be a multiple exponential, but this is not the case for a semi-simple $\hat{H}_{eff}$. If the ergodic properties permit decay, and the initial state is deep in B , the decay rate starts at zero at $t=0$ and remains zero for a period while the packet broadens and moves towards T ; the rate of decay then rises to a maximum and falls off, perhaps in a non-monotonic fashion. This behavior derives from the noncommutation of $\hat{H}_{BS}$ and $\hat{H}_D$ (nonnormality of $\hat{H}_{eff}$). The probability of finding the molecule in B is

$$\begin{aligned} W_B(t) &= {}_t\langle\psi_B|\psi_B\rangle_t \\ &= \sum_E \sum_{E'} c_E c_{E'}^* e^{-i(E_R - E'_R)t/\hbar - (E_I - E'_I)t/\hbar} \end{aligned} \quad (66)$$

The phases (for $E \neq E'$) can introduce coherence effects into the decay process.

Of course, to evaluate the properties of $\hat{H}_{eff}$ one must know $\hat{H}_{BS}$ and $\hat{H}_D$; given $\hat{H}$ this means choosing $\hat{P}_B$, which implies knowledge of the eigenstates of $\hat{H}$, and this is just what is not usually available. A simple, crude, model can be constructed by choosing $\hat{H}_{BS}$ and $\hat{H}_D$ classically. Nordholm and Rice considered a two oscillator coupled system for which

$$\begin{aligned} H_{classical} &= \frac{1}{2}(\dot{p}_1^2 + A_1 q_1^2) + \frac{1}{2}(\dot{p}_2^2 + A_2 q_2^2) - \lambda q_1^2 q_2, \quad q_1 < q_c, \\ &= \frac{1}{2}(\dot{p}_1^2 + A_1 q_c^2) + \frac{1}{2}(\dot{p}_2^2 + A_2 q_2^2) - \lambda q_1^2 q_2, \quad q_1 > q_c. \end{aligned} \quad (67)$$

Thus, one oscillator has a cutoff at, say, E_c . Even without the cutoff $H_{classical}$ describes a system that can dissociate, say at $E = D$. $\hat{H}_D$ is diagonal in the states of $\hat{H}(\lambda=0)$ for $E < D$:

$$\begin{aligned} \hat{H}_D |m_1, m_2\rangle &= d(m_1) |m_1, m_2\rangle, \\ d(m_1) &= 0, \quad \hbar\omega(m_1 + \frac{1}{2}) < E_c = \frac{A_1}{2} q_c^2; \quad d(m_1) > 0, \quad \hbar\omega(m_1 + \frac{1}{2}) \geq E_c. \end{aligned} \quad (68)$$

$d(m_1)$ should be calculated, e.g. by Fano's method. Instead, in the crude model $d(m_1)$ is estimated from the classical half-life. The specification of $\hat{H}_{eff}$ is now complete; $\hat{H}_{BB}$ and $\hat{H}_D$ can be obtained in matrix form using the basis states $|m_1, m_2\rangle$. The results of a calculation for which $(E_c/D) = 0.48$ are:

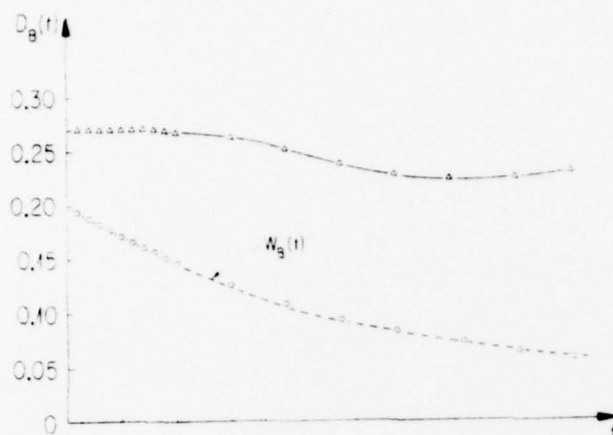
- (i) E_I varies over a wide range even for $E > E_c$. The range of variation is larger when the oscillators are nondegenerate; the variation is irregular.
- (ii) The states $|0, m_2\rangle$ remain very much localized even at high energy.
- (iii) Small values of E_I are associated with local (nonergodic) states; large values with global (ergodic) states.
- (iv) Coherence effects lead to variation in the rate of decay as a function of t .
- (v) Initial states deep in the bound region tend to decay in a nonmonotonic fashion; initial states in the transition region decay monotonically. (See Fig. 15).

The results displayed in Fig. 15 are simply interpreted. An isolated resonant state--one generated by embedding a zero order discrete state in a zero order continuum--decays with a constant lifetime (inverse rate). The population decays displayed in Fig. 15, corresponding to different initial states, are monotone, but the rates of decay are not. The variation of the rates of decay is a consequence of competition between energy transfer to the stable oscillator and fragmentation of the unstable oscillator. Clearly, the more effective the localization of energy in the stable oscillator, and the more efficient the energy transfer relative to reaction, the greater should be the variability of the decay rate, just as observed.

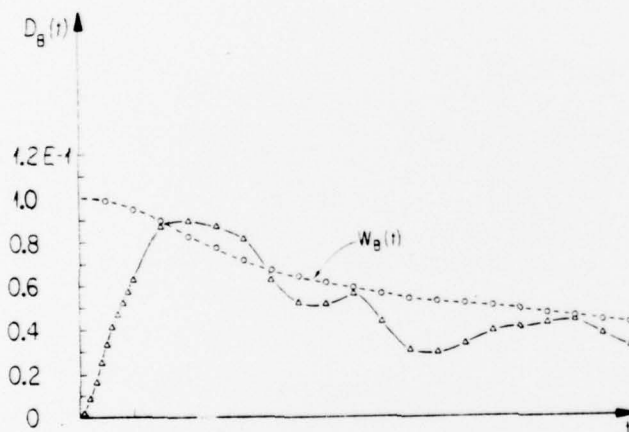
Parr and Kupperman [22] have studied, using classical mechanics, the sensitivity to variation of the initial energy of the rate of fragmentation of the model triatomic molecule M_3 . They find that with initial energy $E < 1.58D$ in a bond of M_3 that does not break, there is delayed fragmentation. The energized M_3 molecule undergoes several (sometimes as many as 20 - 30) vibrations during which time energy accumulates in the other two bonds, which then break. Moreover, the rate of fragmentation is extremely sensitive to small variations in the initial energy (see Fig. 16), and is not a monotone function of the initial energy. Similar results are found for a model of $CRNO$. And, inclusion of rotational motion, and vibration-rotation interaction, does not alter the high sensitivity of the lifetime of the energized molecule to small perturbations in the lifetime of the energized molecule to small perturbations in the initial energy. Parr and Kupperman conclude that there is not, in general, continuity of classical mechanical molecular lifetimes even on the smallest scale of energy differences in the corresponding quantum mechanical case. It is not clear to me that the sources of the nonmonotone rates of decomposition in the Nordholm-Rice and Parr-Kupperman models are the same, but the similarity in findings is striking. Both results clearly suggest that even when intramolecular energy transfer is rapid relative to chemical reaction the reaction rate may not be adequately described by a statistical model.

A rather different approach to the study of fragmentation dynamics has evolved from the theory of radiationless transitions [2]. In this approach no attempt is made to directly study the molecular dynamics. Rather, a spectrum of zero order states and their couplings are postulated, and this spectrum is assumed to incorporate all the necessary information about the molecule. The dynamical behavior of the system is then described by following the amplitude of an initially excited zero order level of the spectrum as a function of time. The calculations can be carried out exactly for several different

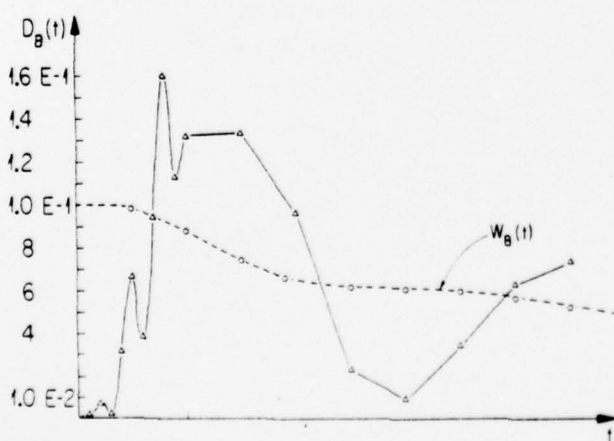
Fig. 15 Probability and rate of reaction for Nordholm-Rice Markoffian model. In the units used $D = 6\hbar\omega$.



a. Initial excitation
 $m_1 = 0, m_2 = 8\hbar\omega$.



b. Initial excitation
 $m_1 = 4\hbar\omega, m_2 = 4\hbar\omega$.



c. Initial excitation
 $m_1 = 8\hbar\omega, m_2 = 0$.

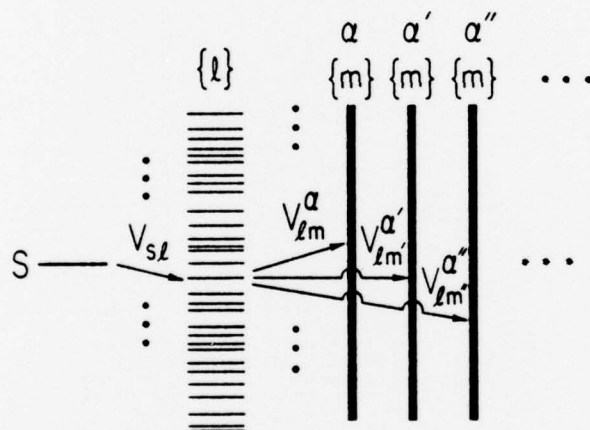
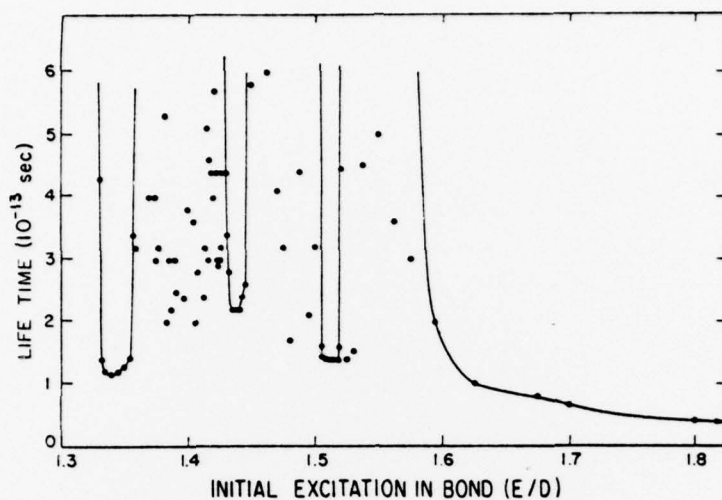


Fig. 16. Lifetime of metastable anharmonic M_3 as a function of the initial potential energy localized in bond 2. Bonds 1 and 3 break, eventually. From [22].

Fig. 17. The skeleton spectrum of the Heller-Rice model. Each continuum m, α represents a different partitioning between relative translational energy and internal energy of the products.

assumed energy dependences of the matrix elements coupling the different zero order manifolds. It is amusing to note that what is widely accepted as intuitively plausible with respect to the behavior of these coupling matrix elements can lead to dynamical behavior which is very different from that obtained from integrating the equations of motion under conditions widely accepted as intuitively plausible with respect to energy exchange between oscillators.

Consider the model spectrum of states shown in Fig. 17. It is assumed that the system is prepared by excitation of the zero order state φ_s . This state is not directly connected to the fragmentation continuum. Rather, φ_s is coupled to the intermediate dense manifold of zero order levels $\{\varphi_l\}$, and these in turn are coupled to the several continua $\{\varphi_m^a\}$. This spectrum is designed to model a situation in which the initially prepared state must relax to a different state before reaction occurs. The usual expectation, derived from chemical kinetic arguments, is that the population of φ_s will decay sequentially to the continuum via intermediate buildup and decay of population in the manifold of levels $\{\varphi_l\}$. The simplest assumption that can be made about the coupling matrix elements of this spectrum is that they are constants independent of the energy [40], [41]. The dynamics of decay of φ_s under this assumption deviate grossly from what is expected from the kinetic arguments cited. Because the matrix elements are constant, amplitude flows coherently from φ_s to the $\{\varphi_l\}$ and from the $\{\varphi_l\}$ to the $\{\varphi_m^a\}$, and interference between the coherent amplitude components in the many levels leads to parallel feeding of the intermediate and fragmentation manifolds. There is not, in this case, a buildup and subsequent decay of amplitude in the levels $\{\varphi_l\}$, and a buildup of amplitude in the continua $\{\varphi_m^a\}$. Even though the assumed constancy of the coupling matrix elements does not appear to be qualitatively incompatible with molecular properties, it leads to decay kinetics which are peculiar.

Since the peculiar coherence effects just described arise from the assumption that the coupling matrix elements are constants, and since no molecule is likely to have this property, the consequences of other assumptions should be studied. Heller and Rice [42] have examined the consequences of assuming that $V_1 \equiv V_{sl}$ and $V_2 \equiv V_{lm}^a$ have random character. The dynamics have been worked out for the case of many coupled continua, with each molecular level coupled to each continuum.

The difference between constant and random coupling models arises as follows: For constant coupling flux from φ_s into $\{\varphi_l\}$ appears "near" the V_{lm}^a coupling region but escapes almost as soon as it enters $\{\varphi_l\}$, i.e. constant coupling leads to a steady state situation in which the flux into the " V_{lm}^a coupled" region from φ_s is equal to the flux out, hence both $\{\varphi_l\}$ and $\{\varphi_m^a\}$ serve as escaping continua in the sense that there is a flow out of a local interaction region into a non-interactive asymptotic region simultaneously in both manifolds. Thus, constant coupling has the effect of reducing the entire dense manifold, with all its symmetry variations, to the status of a single escaping translational continuum. In the random coupling case sequential behavior is obtained because there is an incoherent flow from φ_s into $\{\varphi_l\}$, and the flux appears "uniformly in all of $\{\varphi_l\}$." Because of the uniformity of the flow into $\{\varphi_l\}$ there is a linear buildup in the $\{\varphi_l\}$ to $\{\varphi_m^a\}$ manifold coupling. For t small the probability of dissociation then builds up as t^2 , which is characteristic of sequential flow. Note, for this to be true only V_{sl} V_{lm}^a need be random, not V_{sl}, V_{lm}^a separately. We note in passing that although the random coupling model predicts a

sequential kinetic decay as expected, and a branching of population into the several fragmentation continua, there is no a priori reason why that final branching ratio need be statistical. However, when $\langle (V_{nm}^a)^2 \rangle$ is independent of a the branching is determined by the relative values of the densities of states in the several continua $\{\rho_m^a\}$.

The two examples cited represent extremes in the possible behavior of the matrix elements. Little is known of more general cases. Muthukumar and Rice [43] have studied the consequences of the assumption that there are both systematic functional and random coupling matrix elements; the former were treated as a perturbation of the latter. As particular examples they analyzed mixing of constant coupling and random coupling, and the mixing of Lorentzian coupling and random coupling. As expected, interference effects alter the time dependence of the decay of the system. For the case of mixed constant and random coupling these interference effects can increase or decrease the width of the resonance, i.e. the time scale of the decay, depending on subtle variations of the ratio of magnitudes of the matrix elements. Also, the time dependence is no longer simple. For small t one finds a linear combination of t and t^2 terms characteristic of nonsequential and sequential decays, but the general behavior in time is more complex. The case of mixed Lorentzian coupling and random coupling is designed to mimic the situation when a few matrix elements are more important than others, but none can be neglected. That is, there is tight coupling within some subset of levels, which in turn are embedded in a dense manifold of levels. The calculated time evolution of the population of the initially excited level exhibits two time constants for small t , and is rather complex for large t . The shorter time constant corresponds to the redistribution of energy amongst levels which are nearly resonant with the initially excited level, and the longer time constant corresponds to the relaxation to other levels.

Consideration of the behavior of the coupling matrix elements of a model spectrum such as shown in Fig. 17 inevitably leads to the question: When can a Master equation be used to describe intramolecular dynamics? I do not believe we have the answer to this question, although sufficient (but not necessary) conditions for the validity of a Master equation have been established. In the most complete of the attempts to derive a Master equation for a strongly coupled finite system of oscillators, Kay [44] starts with the usual decomposition of the Hamiltonian, $H = H_0 + V$. However, unlike the usual decomposition of H , in this case V must not be small. It is necessary that V simultaneously couple many degrees of freedom and lead to multiple (vibrational) quantum exchanges between the states defined by H_0 , namely, $H_0 |m\rangle = E_m |m\rangle$. Because of the complexity of the system, when the states $|m\rangle$ are ordered according to energy E_m , it is to be expected that the character of $|m-1\rangle$, and of $|m+1\rangle$, will differ considerably from that of $|m\rangle$. This is taken to be a qualitative feature of the many oscillator system.

Kay argues that three important energy ranges characterize the many oscillator system:

- (a) ΔE : Let the coupling be measured by $V_{nm} \equiv \langle n | V | m \rangle$. It is assumed that V_{nm} and the vibrational density of states is sensibly constant over the energy interval ΔE .
- (b) Γ : By virtue of nonzero coupling between the levels of H_0 these levels acquire a mean width Γ .

(c) $g\epsilon$: Let ϵ be the mean spacing between the levels of H_0 , and g a large integer. Kay requires that averages over g adjacent levels be sensibly the same as an average of the same quantity over ΔE .

The three energy ranges (a), (b), and (c) are related as $T \ll \Delta E, g\epsilon \ll T$. A Master equation describes an irreversible process. The required element of incoherence, leading to irreversible flow of energy on the time scale of interest, is introduced by Kay under the assumption that there is no correlation between coupling matrix elements V_{nm} and $V_{nm'}$ for $|m\rangle$ and $|m'\rangle$ less than ΔE apart:

$$g^{-1} \sum_{\substack{n \\ |n-n_0| < g/2}} V_{nm} = 0, \\ g^{-1} \sum_{\substack{n \\ |n-n_0| < g/2}} V_{mn} V_{nm'} = 0 ; m \neq m', |E_m - E_{m'}| < \Delta E. \quad (69)$$

The two expressions of the assumption of incoherence can be combined to read

$$g^{-1} \sum_{\substack{n \\ |n-n_0| < g/2}} V_{mn} V_{nm'} = \nu^2 \delta_{mm'} ; |E_m - E_{m'}| < \Delta E. \quad (70)$$

Condition (70) plays the same role in Kay's analysis as does the condition of diagonal singularity in Van Hove's analysis. There is also a similar condition in the random matrix theory analysis of Gelbart, Rice and Freed [45].

As a final condition Kay postulates that there is strong interconnection of states. This means that any pair of states $|m\rangle, |m'\rangle$ closer in energy than $g\epsilon$ is connected by a chain of couplings through intermediate states $|n_1\rangle, |n_2\rangle, \dots, |n_k\rangle$, such that $V_{n_j n_{j+1}} \neq 0$ for $n_0 = m, n_{k+1} = m'$ and

$$\frac{1}{2}(E_m + E_{m'} - g\epsilon) \leq E_{n_1}, \dots, E_{n_k} \leq \frac{1}{2}(E_m + E_{m'} + g\epsilon).$$

The coupling is characterized as strong interconnection when the intermediate sequences of coupled levels are short enough and numerous enough that all states within $g\epsilon$ are populated on a time scale $t \ll \hbar/\delta$ where $\Gamma \gg \delta \gg g\epsilon$.

With the conditions cited Kay shows that a generalized Master equation describes the evolution of a function related to the occupation probability of a state representing a certain property A, but having zero order energy specified only to ΔE . Transition probabilities connect any g consecutive levels in ΔE . Because V is not small transitions do occur between states with different energies.

V. Some Inferences from Experiment

I remarked earlier that although there exist several sets of experimental data that can be interpreted as indicating intramolecular vibrational relaxation is slower than chemical reaction, the subsidiary assumptions necessary to the drawing of that inference greatly weaken it. In closing, I will cite a very few examples of the kind of experimental data that suggest the reality of nonstatistical behavior in some situations.

(1) Mr. S. Michaelson [46] is completing a study of the dependence of the rate of fragmentation of ClO_2 on initial vibrational and rotational state. Although the 400 level of the ClO_2 state is 2082 cm^{-1} higher in energy than the 100 level, the rate of predissociation is essentially the same. In contrast, although it has only 283 cm^{-1} more energy, predissociation from the 110 level is much more rapid than from 100, and also more rapid than from 400. Also, predissociation from the level 010 is more rapid than from 100, although 010 lies 418 cm^{-1} lower in energy. Even though the analysis is not yet complete, these preliminary findings strongly suggest that the fragmentation of ClO_2 from prepared rovibronic levels will not be accurately described by a statistical model.

(2) Cantrall [47] has made a careful analysis of all the available data on multiphoton dissociation of SF_6 . He concludes, after a variety of trial calculations, that the triply degenerate mode ν_3 dominates the absorption process up to an energy $\sim 0.7D$. Although this result supports the notion that up to $\sim 0.7D$ vibrational redistribution in SF_6 is slow on the time scale of absorption, it does not imply that the same is true at the threshold for fragmentation, or above that threshold. The Cantrall conclusion, which refers to the mechanism of absorption of energy, is not in conflict with the conclusion by Lee and coworkers [48] that just prior to fragmentation there is a statistical distribution of vibrational energy in the molecule, (Fig. 18)

(3) Studies by Lee and coworkers [49], and MacDonald and coworkers [50], of the substitution reaction



are consistent with there not being complete randomization of vibrational energy in the intermediate complex $\text{C}_2\text{H}_4\text{F}^*$. This inference is also supported by the theoretical calculations of Zvijac and Light [51], who show that in the evolution from reactants to products a small subset of the total degrees of freedom of the system are tightly coupled to one another everywhere along the reaction path.

(4) When a large aromatic molecule is excited to a vibronic level of a singlet excited state, and intersystem crossing to a lower triplet state occurs, that triplet is "born" with excess vibrational energy. Schlag and coworkers [52] have studied, by a generalized flash photolysis method, the evolution in time of the vibrational distribution generated by radiationless transition following excitation of the lowest singlet state of naphthalene. It is observed that the vibrational distribution created by the radiationless process does not change on the time scale between collisions, which is $\sim 1 \mu\text{s}$. If the radiationless process is intersystem crossing to the lowest triplet that state would have about $11,000 \text{ cm}^{-1}$ excess vibrational energy. The estimated rate of intramolecular vibrational relaxation is rather like that suggested by Tric for quinoxaline with $10,000 \text{ cm}^{-1}$ excess energy. (Fig. 19)

(5) Grant and Bunker [53] have simulated the unimolecular decomposition of C_2H_6 via CC and CH bond scission on a "realistic" energy surface. The results, for several energies and patterns of energization, reveal deviations from the predictions based on statistical behavior of the energized molecule. The interpretation of these results is based on the existence of differences in coupling strength between the various vibrational modes.

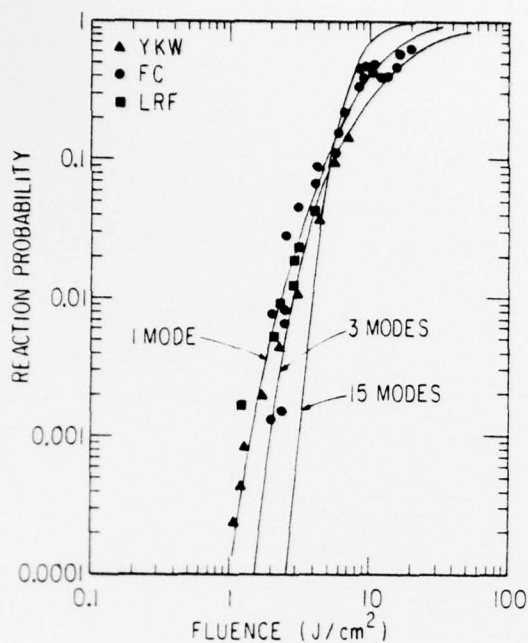


Fig. 18a Reaction probability $P(\Phi)$ of SF_6 versus laser fluence Φ . The symbols and labels refer to different experimental groups. The curves refer to calculations for different numbers of oscillators active in the absorption of energy. From [47].

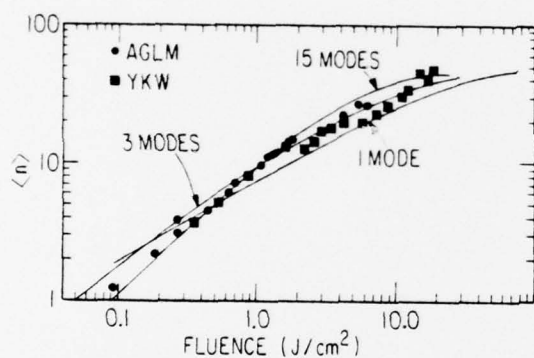


Fig. 18b Mean number of photons absorbed per pulse, $\langle n \rangle$, versus laser fluence for SF_6 . From [47].

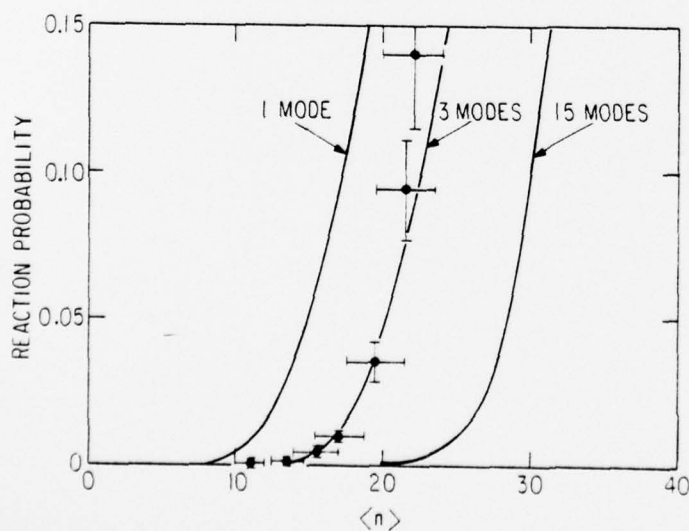


Fig. 18c Reaction probability versus mean number of photons absorbed for SF_6 . From [47].

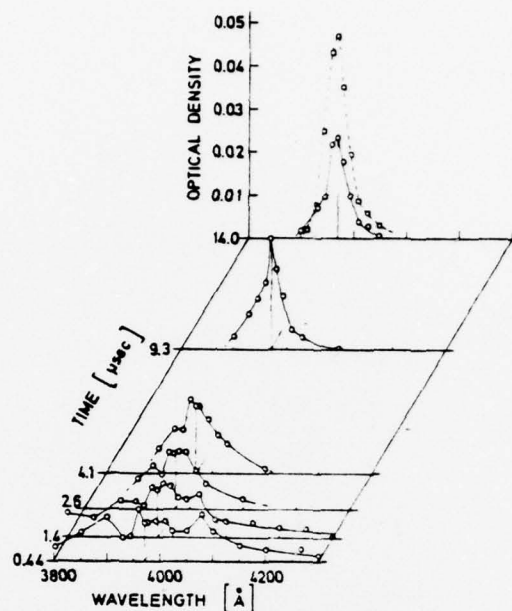


Fig. 19 The time evolution of the $T^* \leftarrow T_1$ absorption spectrum in naphthalene h_8 , subsequent to ISC at low pressure (o) ($p = 68$ mtorr N). The molecules were optically excited to the $8(b_{1g})$ vibronic band of S_1 . For comparison, a "high pressure" $T - T$ spectrum (o) ($p = 68$ mtorr N + 2.5 torr Ar) is given at $14 \mu s$. The time scale is related to the onset of the exciting laser pulse. From [52].

VI. Conclusions

I suggest that what we have learned from the various theoretical approaches described is to not underestimate the complexity and subtlety of the dynamics of strongly coupled oscillator systems. Although neither available experimental data nor the several kinds of theoretical treatments provide unequivocal evidence for slow intramolecular relaxation in real molecular systems, the hint that such can sometimes occur is strong. The principle lesson to be drawn is that there is unlikely to be a universally valid description of intramolecular relaxation and/or fragmentation of isolated molecules. Statistical descriptions of the dynamics will certainly be valid in some energy range and for some time domain, but nonstatistical behavior is to be expected in other cases, for example when the time scale of the process of interest includes competitive relaxation processes. There will be idiosyncratic differences between species, dependent on the nature of the energy dependence of coupling matrix elements, etc. All of these factors must be included in a fully satisfactory theory of chemical reaction rates.

VII. Acknowledgements

The research which this review surveys has been supported over a period of years by the National Science Foundation and the Air Force Office of Scientific Research. It would not have been possible without the collaboration of many talented colleagues. Several of the illustrations in this paper are drawn from the work of others. Specifically, Figs. 2 and 3 are from [8], Figs. 9, 10 and 16 from [22], Figs. 13 and 14 from [30], Fig. 18 from [47] and Fig. 19 from [52].

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