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Energy Redistribution in Molecules in the Quasi-Periodic and Ergodic Regimes

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Abstract

Some results on the classical mechanics of anharmonic vibrations in several-dimensional systems are summarized, and their relation to unimolecular reaction rate theory and to infrared multiphoton dissociation of molecules is discussed. Quantum connections are considered using semiclassical theory.

1. Introduction

The anharmonic behavior of vibrational systems has been the subject of intense classical mechanical investigation in recent years [1], and some of these results and their application will be described in the present paper.

It is known from analytical arguments (KOLMOGOROV-ARNOLD-MOSER Theorem [1]), and further corroborated by numerical studies [1], that at low energies the behavior of anharmonic systems is highly regular. One has "anharmonic modes", characterized by certain constants of the motion, the action variables J_i [2]. Thereby, the region of the phase space occupied by any stable system in this energy region in the long-time motion is determined by the J_i's (or in a degenerate case by one or more canonically conjugate angle variables also [2]). At high energies, numerical studies indicate that the size of the phase space region covered by the trajectory is determined, instead, only by the total energy (and presumably in 3-D by the angular momentum J_ϕ and any of its space-fixed components J_z). We shall term the low and high energy regions "quasi-periodic" and "ergodic," respectively, and consider implications for unimolecular reactions and for infrared multiphoton dissociation.

2. Description of "Quasi-periodic" and "Ergodic" Regimes

Considerable insight into the behavior of anharmonic systems is obtained from classical mechanical trajectories. The latter in turn are computed by numerically integrating Hamilton's equations of motion using the Hamiltonian for the system. An example of a trajectory for the Hamiltonian

$$H = \tfrac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y y^2) + \lambda x(y^2 + yx^2), \qquad (2.1)$$

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where p_x and p_y are the x and y components of momentum, is given in Fig. 1 of [3]: At low energies the trajectory sweeps out, when ω_x and ω_y are incommensurate, a rectangular-like region in xy space, the boundaries of the "rectangle" being termed the "caustics". The "rectangle" is contained within a curve for which $H = E$ (an ellipse-shaped curve) and touches it at the four corners of the "rectangle". Thus, the trajectory under these conditions does not cover all of the configuration space energetically accessible to it. At these energies where such trajectory figures are obtained, action variables J_i (cyclic pdq path integrals along a path q) can be defined and computed, e.g., as in [3-9].

In contrast, in the high energy regime the trajectory appears to cover the available configuration space (and indeed the energetically available phase space), and to depend only on the energy E, and in 3-D also on J_ϕ and J_z. Thus, the long-time statistical behavior of the system is very different in the two energy regimes: in the quasi-periodic case only a limited portion of the energetically accessible phase space is sampled, for any given value of J_i's.

When there is an internal resonance in the system, e.g., when ω_x equals ω_y in (2.1) (a 1:1 degeneracy) the behavior is quite different: in the case of $\omega_x = \omega_y$ and $\lambda = 0$ the trajectory is a periodic one, an ellipse. Whereas, with $\lambda = 0$, the trajectory thereby covers a "one-dimensional" domain, in the case of $\lambda \neq 0$ it ultimately covers a two-dimensional region. An example is given in Fig. 3 of [5], which uses (2.1) with $\omega_x = \omega_y$. Here, the trajectory sweeps out a two-dimensional circular region, as a result of precession of the ellipse due to the anharmonic coupling term.

There is thus a marked contrast in energy sharing behavior between the trajectories for incommensurate ω_x and ω_y and for $\omega_x = \omega_y$. In the first case the y- amplitude (i.e., the vertical distance between parallel "caustic" lines) hardly varies with time. Thus, there is relatively little interchange between the "energies" of the x- and y-degrees of freedom. The zeroth order action variables J_x^0 and J_y^0 are almost constant. In the $\omega_x = \omega_y$ case, the system is sometimes vibrating mainly along the x-direction, sometimes mainly along the y-direction, and sometimes in between. Thus, in this case there is extensive energy exchange between the x- and y-degrees of freedom. The unperturbed constants J_x^0 and J_y^0 are no longer even approximately constants of the motion, although certain related unperturbed constants J_r^0 and J_θ^0, based on polar coordinates, can be approximately constant in the perturbed system. Similarly, trajectories for a 2:1 resonance (Fermi resonance where $\omega_x = 2\omega_y$) show significant energy sharing [10,11].

Energy sharing certainly occurs in the ergodic regime, but as discussed above it can also occur in the quasi-periodic regime between degrees of freedom for which there is an internal resonance. However, in the latter case there are constraints, e.g., in the 1:1 resonance the maximum amplitude for a given energy depends on one of the action variables. There is no such constraint in the ergodic case.

The phase-averaged behavior in the quasi-periodic regime is characterized by the action variables, and that in the ergodic regime only by the energy, and in 3-D also by the angular momentum and by one of its components. Since the behavior in the quasi-periodic and ergodic regimes can be quite different, it is useful to examine a characterization of some of these differences. They occur in (1) the "Poincaré surfaces of section", (2) the rate of separation of adjacent trajectories with time, and (3) the vibrational spectrum associated with trajectory. We consider each of these differences in this order.

A Poincaré surface of section [1] is a plot wherein each time a trajectory crosses, say, the $y = 0$ line with $\dot{y}>0$ the value of p_x and of x is recorded. Such a plot for the system discussed earlier in the quasi-periodic case with incommensurate ω_x and ω_y gives a series of points which ultimately form an ellipse, as in Fig. 3 of [3]. The value of J_x is obtained by evaluating the area, $\oint p_x dx$, of such a plot. The same value for J_x would be obtained for points for which $\dot{y}<0$, and also at any other line y = constant, as long as that line crosses the same caustics. Similarly, each time the trajectory crosses the line $x = 0$ one obtains J_y from a plot of p_y versus y. In the case of resonance systems (e.g., $\omega_x = \omega_y$ and $\omega_x = 2\omega_y$) it was useful to introduce curvilinear surfaces of section so as to obtain Poincaré surfaces which correctly intersected the caustics [5,10,11].

In the case of the ergodic regime, the Poincaré surface of section displays a shotgun pattern [1], rather than forming the smooth "curve" which characterizes the quasi-periodic case, and the simple phase integrals $\oint pdq$ (action variables) are believed to be undefined.

In the quasi-periodic regime adjacent trajectories separate on the average (in an oscillatory way) linearly with time, while in the ergodic regime the separation is exponential [1]. Some question on the use of this criterion for distinguishing between the two regimes has been raised in [12].

The vibrational spectra associated with the trajectories in the two different regimes are described in the next section.

3. Vibrational Spectra

Recently, the spectral intensity function $I(\omega)$ associated with the vibrational trajectory has been computed [13]. The spectral intensity for any function μ of coordinates and momenta is related to the autocorrelation function $\langle\mu(0)\mu(t)\rangle$ in a standard Fourier integral manner. For purposes of calculating $I(\omega)$ from trajectories, it was shown that [13]

$$I(\omega)= \frac{1}{2\pi} \lim_{T\to\infty} \frac{1}{T} \left|\int_0^T \mu(t) \exp(-i\omega t)dt\right|^2 . \qquad (3.1)$$

The behavior in the quasi-periodic regime is characterized by the property that any function of coordinates and momenta can be expanded in a Fourier series containing a number of fundamental frequencies equal to (or less) than the number of coordinates, and containing combinations and overtones thereof [2]. The number of fundamentals is less only in exactly degenerate systems. The spectrum described by $I(\omega)$ is thereby a line spectrum, as in Fig. 3 of [13] for the Hamiltonian (2.1). Line spectra were also found in our studies for the other quasi-periodic systems, such as those for the 1:1 and 2:1 resonances.

In the quasi-periodic regime the spectral intensity function $I(\omega)$ depends on the initial conditions, e.g., on the values of the action variables J_x and J_y at any given energy: The magnitude of $I(\omega)$ at an ω equal to the frequency for the x-motion in the $\omega_x \neq \omega_y$ case is small when J_x is small and conversely. The frequencies themselves also depend somewhat on the J's, because of the anharmonicity.

In the ergodic regime the spectrum is different in two respects: it is "broadened" [13,14] and, at any given initial energy, it is approximately independent of initial conditions. (It would be exactly independent if T in (3.1) were large enough and if the system were really in the ergodic regime.) The "broadened" spectrum appears to consist of many lines, which may reflect the presence at these high energies of many internal resonances. CHIRIKOV has postulated, in fact, that ergodicity arises from the overlap of internal resonances [15], and has suggested a semiquantitative criterion for onset of ergodicity.

We consider next some quantum aspects of these classical results, using both semiclassical and quantum calculations.

4. Quantum Aspects

In the quasi-periodic regime, the existence of the action variables permitted semiclassical methods to be used to obtain the quantum mechanical eigenvalues [3-11]. It was possible, for example, to evaluate two topologically independent $\oint pdq$ integrals, i.e., the action variables, from trajectory data described in Sec. 2 for a two degree of freedom system, either by integrating along the caustics or by evaluating the areas of the Poincaré surfaces of section [3-5]. The second method has been extended to higher dimensions [14,16]. Setting these integrals equal to their semiclassical values $(n_x + \frac{1}{2})h$ and $(n_y + \frac{1}{2})h$ for vibrations, an iteration procedure led to integral values of the quantum numbers n_x and n_y. The eigenvalues for the energy are the energies for which n_x and n_y are simultaneously integers. The agreement between these semiclassical eigenvalues and the quantum mechanical ones was reasonable, and other methods have also been presented [6-9]. Both nonresonant [3] and resonant [5,11] cases can be treated by the trajectory method.

In the quasi-periodic case the region occupied by the trajectory, i.e., the region bounded by the caustics, describes the "classically-allowed" region for the wavefunction for the given eigenstate. Inside the caustics the wavefunction is oscillatory and outside the caustics it vanishes exponentially. When, as in the Fermi resonance case, this classically-allowed region was curvilinear in shape (a bent rectangle), the region occupied by the oscillatory portion of a purely quantum mechanically calculated wavefunction occupied a similarly shaped region [11,14].

To obtain semiclassically from trajectories the frequency appropriate to a quantum mechanical transition $(n_x,n_y) \rightarrow (n_x+1, n_y)$, it sufficed, by a correspondence principle argument, to obtain the relevant classical frequency corresponding to a classical state $(n_x+\frac{1}{2}, n_y)$. It agreed well with the quantum mechanical frequency for the above transition, calculated using a large basis set to locate the eigenvalues. (It also sufficed, in the process, since the perturbation was not very large, to use a trajectory corresponding to the relevant values of zeroth order action variables.) Similar remarks applied to the other transitions [13].

This spectral method for eigenvalue differences, i.e., for frequencies, is much faster computationally than that of the direct determination of the individual eigenvalues. An example for a system with a Hamiltonian of the form (2.1) but for three degrees of freedom is given in Table II of [13], and the agreement was quite reasonable.

In the ergodic regime on the other hand, it has not been possible thus far to calculate eigenvalues semiclassically. Nevertheless certain classical and quantum properties can be compared. The wavefunction shows some tendency to occupy all of the classically-allowed region energetically accessible, just as the ergodic trajectories did, and further calculations are in progress [11]. This behavior contrasts with the behavior of the wavefunction in the quasi-periodic regime described earlier, where both the trajectory and the wavefunction "occupied" a region determined by the individual action variables rather than only by the total energy (and, in a 3-D system, by angular momentum and one of its components). Some predictions of other aspects are given in [17].

A comparison of the classical and quantum spectra in the ergodic regime is also of interest. In the absence of well-defined action variables J_x and J_y in the ergodic regime, a procedure similar to that used in the quasi-periodic case has not yet been devised for calculating an ergodic regime spectrum semiclassically. A rather oversimplified procedure of choosing an energy region $E \pm \hbar\omega$, where ω is the largest frequency and then calculating all possible quantum mechanical transition frequencies for energy levels in that energy domain has been explored [14]. It yields a number of spectral lines which are in the same region as those in the ergodic classical spectrum, and with somewhat related intensities, but much fewer in number. Thus, there is some connection between quantum and classical spectra in the ergodic regime, but details are not yet well understood. The similarities do suggest that classically-computed trajectories for infrared multiphoton dissociation are useful for understanding dynamical aspects of that process.

We turn next to some implications for unimolecular reactions and for infrared multiphoton dissociation.

5. Implications for Unimolecular Reactions

For unimolecular reactions one can envisage two limiting forms of a theory, ergodic and quasi-periodic [18]. In the ergodic regime the long-time behavior of a bound state system, we saw, is determined by its energy E, total angular momentum J_ϕ and any component J_z, and similarly for a dissociating system. A dissociation rate constant $k(E,J_\phi,J_z)$ for such a system depends on those constants. In a strong collision theory the unimolecular reaction rate constant k_{uni} is then given as a function of pressure p and temperature T by

$$k_{uni}(p,T) = \int\ldots\int k(E,J_\phi,J_z)\,\rho(E,J_\phi,J_z,T)\,dE\,dJ_\phi\,dJ_z/[1+k/\omega p], \qquad (5.1)$$

where $\rho(E,J_\phi,J_z,T)dEdJ_\phi dJ_z$ is the thermal equilibrium probability of finding the molecule in the interval $(E,E+dE)$, $(J,J+dJ)$ and (J_z,J_z+dJ_z), and ω is the deactivation collision rate per unit pressure. RRKM theory [19-22] uses (5.1) together with equilibrium statistics to calculate ρ and transition state theory to calculate k.

In the quasi-periodic regime the long-time behavior of a bound state system we saw, is determined instead by its action variables, whose totality is denoted by J and two of which are J_ϕ and J_z. When a molecule is in an unbound state (i.e., dissociates) only J_ϕ and J_z among the J's are precisely defined. Thus, use of the other J's becomes an added approximation, even if the molecule behaves most of the time in some quasi-periodic manner, and even if those J's are defined by simulating the actual potential by a bound state potential. With this approximation for defining the J's, and assuming a kinetic formalism similar to the above for the ergodic case, k would, in a quasi-periodic theory, depend on the J's and be written as k(J). A strong collision unimolecular reaction theory for the quasi-periodic regime yields [18]

$$k_{uni}(p,T) = \int\ldots\int k(J)\ \rho(J,T)dJ/[1 + k(J)/\omega p], \qquad (5.2)$$

where dJ represents $\Pi_i dJ_i$ and $\rho(J,T)dJ$ is the thermal equilibrium probability of finding the molecule in $(J,J+dJ)$. If k(J) were only weakly dependent on J at the given E,J_ϕ,J_z, one could replace it in (5.2) by its average value, $k(E,J_\phi,J_z)$, i.e., by

$$k(E,J_\phi,J_z) = \int\ldots\int k(J)\ dJ/\int\ldots\int dJ, \qquad \text{at fixed } J_\phi,J_z,E \qquad (5.3)$$

(The integration volume in J-space in (5.3) is r-3 fold dimensional, for a system with r rotational-vibrational degrees of freedom, in virtue of the three constraints.) Integration over J in (5.2) then yields

$$\int\ldots\int \rho(J,T)\ dJ = \rho(E,J_\phi,J_z,T)\ dEdJ_\phi dJ_z \qquad (5.4)$$

for given J_ϕ,J_z,E. In (5.4) the integration is over the J space contained in $dEdJ_\phi dJ_z$. Eq. (5.2) then yields the ergodic regime (5.1).

However, if k(J) fluctuates greatly with J at fixed (E,J_ϕ,J_z) the quasi-periodic and ergodic regime theories could differ substantially as a function of pressure, and some calculations on this aspect are being planned.

N. B. SLATER's theory of unimolecular reactions [23] is a harmonic oscillator approximation to the quasi-periodic theory described by (5.2). His vibrational amplitudes a_i are closely related to the action variables J_i ($J_i \propto a_i^2$ in the harmonic approximation). One major difference arises in the role of degeneracies. If a system is degenerate throughout its motion, its trajectory covers a fewer dimensional region than it would if non-degenerate (as in the case described earlier in Sec. 2 with $\omega_x = \omega_y$ and $\lambda = 0$). Thereby, in such a degenerate case, a SLATER k, averaged at a particular energy, is very different from the ergodic k at that energy. A small amount of anharmonicity to break this degeneracy would void this aspect of the purely harmonic oscillator theory, even apart from the question of whether a quasi-periodic theory for k would be appropriate.

There have been extensive tests of unimolecular reaction rate theory, using thermal rate data and using chemical activation results, e.g. [20-22]. The principal uncertainty in such tests lies in knowing the molecular properties of the transition state for the reaction. Typically, in the case of unimolecular reactions one chooses the properties to be consistent with A_∞, the value of the pre-exponential factor for the limiting high pressure unimolecular reaction rate constant. Since there are a number of vibration frequencies which may be changed substantially when products are formed from reactants, and hence perhaps also when the transition state is formed from reactants, there is a lack of uniqueness in the values of the frequencies of the transition state to be selected so as to be consistent with the value of A_∞. However, it appears that some reasonable latitude in this choice largely leaves the pressure dependence of k_{uni} unaffected, provided the choice always has the same A_∞, e.g., [24].

This relative lack of strong dependence of calculated pressure behavior of k_{uni} on the detailed choice of frequencies, subject to the constraint of consistency with A_∞, is also reflected in the classical limit of the RRKM expression: here, regardless of the values of the uncertain frequencies, there is only one unknown parameter in the classical limit, for a given activation energy and number of transition state vibrational coordinates, and taking, as in RRKM, all vibrations of the molecule to be "active". This unknown parameter is then determined uniquely by A_∞ in this classical limit, and so even in the near-classical case there will be some insensitivity to choice of the transition state frequencies, provided the choice is consistent with A_∞.

The chemical activation and unimolecular reaction rate data find a consistent explanation, using such transition state frequencies [20-22].

Further results on unimolecular reaction rate theory are available from energy distributions of products of molecular beam reactions involving formation of intermediate complexes [25-27]. Here, when the transition state is "loose" there are no "exit channel effects" and the energy distribution in the products becomes a fairly direct test of the energy distribution in the transition state, namely whether or not it is statistical (ergodic) and the test is, importantly, under collision-free conditions. Results for such "loose" transition states tend to support RRKM Theory in the cases studied having large vibrational energy.

There have been many classical trajectory tests of RRKM Theory, e.g., [22,28-30]. RRKM behavior is frequently observed. However, when there are groups of very unequal frequencies, energy sharing between the groups can be slower than otherwise and could be rate determining, depending upon the energy, as expected from the results in Sec. 2.

6. Multiphoton Infrared Dissociation

Recent experimental results in infrared multiphoton dissociation have been interpreted on the basis that the major part of the process occurs in the ergodic regime of the molecule (e.g., use of RRKM Theory) [31,32]; the initial absorption steps are, in effect, in the quasi-periodic regime. The results of trajectory calculations [33] for several-dimensional systems are interesting in this regard. In the quasi-periodic regime one expects the energy of the molecule in the oscillating electric field to be somewhat oscillatory with time, accepting and giving back energy to the electric field. At high energies, when the energy of the vibrationally-excited bond passes more to the other degrees of freedom, and when the molecule also passes into the ergodic regime, the absorption of energy is expected to be less oscillatory. Such behavior is found in the trajectory studies in [33] where a molecule CD_3Cl was simulated (Fig. 4 there).

Various features of the process for CD_3Cl were evident: for the trajectories used (1) the dissociation depended on the energy absorbed rather than on peak power, as in ergodic-type theory [31]; (2) the energy distribution tended to be equilibrated among the various degrees of freedom in 10^{-11} sec, shortly after the pulse began to decay away; during the pulse the distribution was nonrandom, being very high in energy in the pumped mode; (3) the use of two laser pulses produced enhanced dissociation, a weak pulse being on resonance and a strong one off resonance. Results (1) and (3), and equilibration in (2), are consistent with experimental results in other systems.

One may well inquire, however, what significance the classical trajectory results imply in a quantum world. The remaining portion of this paper will be devoted to this question, and in particular to the way in which the molecular energy changes with time. If H_m is the Hamiltonian of the molecule (the total Hamiltonian H being H_m plus the field-molecule interaction) the molecular energy at time t will be defined as $E_q(t)$:

$$E_q(t) = \int \psi^*(q,t)\, H_m(\underset{\sim}{q},\underset{\sim}{p})\psi(q,t)dq, \tag{6.1}$$

where q denotes the totality of coordinates (which we'll choose as "angle" variables) and p are canonically conjugate action variables. $\underset{\sim}{q}$ and $\underset{\sim}{p}$ denote the approximate corresponding quantum mechanical operators [34].

The semiclassical wavefunction can be written as [35]

$$\psi(q,t) = (\partial q_0/\partial q)^{\frac{1}{2}} \exp\,(i\, W/\hbar) \tag{6.2}$$

where $\partial q_0/\partial q$ is a determinant, q_0 is the initial value of q, W is the solution of the time-dependent Hamilton-Jacobi equation, and equals (one can show)

$$\begin{aligned} W(q,t) &= \int_{t_0}^{t} (p\dot{q}-H)\, dt' + p_0 q_0 - H(t_0)t_0 \\ &= \int_{q_0}^{q} p dq - \int_{t_0}^{t} H(t')dt' + p_0 q_0 - H(t_0)t_0, \end{aligned} \tag{6.3}$$

where terms such as $p\dot{q}$ are an abbreviation for a sum $\Sigma p_i \dot{q}_i$ over coordinates. Eq. (6.2) is the wavefunction if interferences are neglected. These interferences result from the occurrence of several branches of W [35] and hence of ψ, which in turn arise when q is not a monotonic function of q_0, e.g., when the determinant $\partial q_0/\partial q$ changes sign.

Introduction of this wavefunction into (6.1) yields

$$E_q(t) = \int H_m(q,p)\; dq_0, \tag{6.4}$$

when W is real-valued in the integration region (no "tunneling"). This E_q is seen to involve an integration of $H_m(q,p)$ at time t over the initial phases q_0, and is none other than the average classical energy E_c of the molecule (averaged over initial phase) at time t. Thus, under the above approximations one has

$$E_q(t) = E_c(t), \tag{6.5}$$

a result which is not surprising in virtue of the approximations made (no interferences and no "tunneling").

A numerical comparison of quantum and classical calculations of the energy absorbed, averaged over a pulse, has been described as a function of the field frequency for systems with one degree of freedom [36]. The results were fairly similar, apart from the occurrence of some quantum "resonances" which might be a reflection of neglected interferences. Clearly numerical comparisons of quantum and classical calculations for higher-dimensional systems are desirable.

In conclusion, one caveat in the use of (6.5) may be raised. A wavefunction such as (6.2) is well behaved in a quasi-periodic regime. At high energies the ergodicity leads to a very scrambled nature of the trajectories. (A laminar travelling vibrational wave in the quasi-periodic regime thus presumably becomes a turbulent one in the ergodic regime.) This trajectory behavior probably also leads to numerous places where $\partial q_0/\partial q$ changes sign, and so to many terms in the semiclassical wavefunction. These would give rise to interferences (e.g., cross terms in $\psi^*\psi$) in computing an integral such as (6.1), interferences which would tend to cancel because of their large number. If so, one would then again be left with (6.5). Semiclassical theory in the ergodic regime remains to be better understood, however. For example, although there are now a variety of techniques for calculating eigenvalues of nonseparable vibrational systems in the quasi-periodic regime, there doesn't appear to be a successful semiclassical calculation of an eigenvalue in the ergodic regime.

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