

A spectral analysis method of obtaining molecular spectra from classical trajectories

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(Received 30 March 1977)

Vibrational classical trajectories of anharmonic molecules are used here to obtain the classical vibrational autocorrelation function and, via a Fourier transform, the power (or infrared) spectrum of the dynamical variables. In the vibrationally quasiperiodic regime the spectrum consists of sharp lines, for any given initial amplitude. The initial amplitudes are chosen semiclassically. The spectral lines are compared with quantum mechanical calculations for systems with two and three coordinates, with excellent agreement. The method is also useful for obtaining a classical spectrum in the ergodic regime; the spectral lines are then "broad" rather than narrow. The method can be used in the analysis of trajectories for unimolecular reactions, infrared multiphoton dissociations, and for obtaining molecular spectra from force fields. The spectral analysis itself has implications for the theory of unimolecular reactions.

I. INTRODUCTION

Many years ago Einstein¹ proposed a quantization of systems not permitting separation of variables: One finds canonical invariants, namely, the action variables² J_i , and quantizes them

$$J_i = \oint \mathbf{p} \cdot d\mathbf{q} = n_i h, \quad (1.1)$$

where the different J_i 's are obtained by integrating over topologically independent paths; $\mathbf{q} (\equiv q_1, q_2, \dots, q_N)$ and $\mathbf{p} (\equiv p_1, p_2, \dots, p_N)$ denote canonically conjugate coordinates and momenta. The theory was further developed by Keller,³ who showed how fractional terms arose

$$J_i = \oint \mathbf{p} \cdot d\mathbf{q} = (n_i + \delta_i) h, \quad (1.2)$$

where δ_i is a known constant, usually being 0 or 1/2, depending on the degree of freedom. He further showed how to evaluate these integrals for a number of nonseparable systems which had zero potential energy within a confined region, on the boundary of which it rose to infinity.

Eastes and Marcus,⁴ and Noid and Marcus⁵ showed how to evaluate these action integrals in nonseparable systems having smoothly varying potential energy functions, and evaluated the eigenvalues semiclassically using Eq. (1.2). The systems treated were both those which were nondegenerate in zeroth order^{4,5(a)} as well as those degenerate in zeroth order.^{5(b)} (The trajectories for the two sets of systems are markedly different.) More recently, other methods have been described.⁶ All of these results refer to systems which are quasiperiodic, i.e., systems for which angle-action variables exist. (In the ergodic regime the action variables do not exist.)

During the course of the present work on these systems it occurred to us that vibrational and vibrational-rotational spectra, that is, the differences of eigenvalues, could be obtained directly, merely by using the vibrational trajectory to obtain a suitable autocorrelation function and then Fourier transforming the latter to obtain the spectrum. According to Bohr's correspondence principle,² the mechanical frequencies are equal to the differences of eigenvalues $(E_m - E_n)/h$, and

provide the spectral lines directly when the appropriate autocorrelation function is calculated.

At low energies in nonseparable anharmonic systems a quasiperiodic behavior has been observed in numerous trajectory studies in the astronomical literature⁷ and is supported by the fundamental theory of Kolmogorov, Arnold, and Moser.⁸ Under such conditions the spectrum consists of sharp lines. At high energies an ergodicity occurs, and so the action-angle variables are no longer good variables. Thereby quasiperiodicity breaks down, and one no longer expects a line spectrum classically for the molecule.⁹ Indeed, we have found that the lines do "broaden" in the ergodic regime.

The spectral analysis method, presented earlier in a recent thesis,^{5(b)} is described in the present paper. Subsequent applications of the present work have recently been made to unimolecular reactions¹⁰ and to infrared multiphoton dissociation.¹¹

II. SPECTRAL ANALYSIS METHOD

The spectral analysis method can be applied to any autocorrelation function, e.g., of coordinates $x(t)$ or $y(t)$, momenta $p_x(t)$ or $p_y(t)$, or any dynamical variable, e.g., the dipole moment $\mu(t)$. Below we shall use $x(t)$ to denote any of these.

$I(\omega)$, the infrared absorption band shape function, or in the case of any dynamical variable $x(t)$ the power spectrum or spectral density, is related to the Fourier transform of its autocorrelation function $C(t)$ in the well-known way¹²

$$I(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} C(t) \exp(-i\omega t) dt, \quad (2.1)$$

where

$$C(t) = \langle x(0)x(t) \rangle. \quad (2.2)$$

The average $\langle \rangle$ indicates an average over an ensemble appropriate to the problem, an ensemble which we describe later. $C(t)$ has the stationarity property

$$\langle x(0)x(t) \rangle = \langle x(\tau)x(t+\tau) \rangle \quad (2.3)$$

and, since $x(t)$ is real, the property of being an even function of t ¹³:

$$C(t) = C(-t). \quad (2.4)$$

This power spectrum (2.1) is related to a certain time average¹⁴

$$I(\omega) = \frac{1}{2\pi} \lim_{T \rightarrow \infty} \frac{1}{2T} \left\langle \left| \int_{-T}^T x(t) \exp(-i\omega t) dt \right|^2 \right\rangle. \quad (2.5)$$

Actually, these two quantities differ by a term which vanishes when $T \rightarrow \infty$ for an ergodic system¹⁵ and which for a quasiperiodic system can be shown to vanish also.¹⁶

In the quasiperiodic regime $x(t)$ can be expanded as a multiply periodic function of N angle variables w_i , in the N -coordinate system. The w_i vary linearly in time and are canonically conjugate to the action variables J_i .²

$$2\pi w_i = \omega_i t + \varphi_i, \quad i = 1, \dots, N. \quad (2.6)$$

In a nondegenerate case the frequencies ω_i are all non-zero and incommensurate. In the degenerate case one can choose the frequencies ω_i ($= \partial E / \partial n_i$) so that a certain number of them, r say, are nonzero and incommensurate, and the remaining ones are zero, in an $N - r + 1$ -fold degenerate system.² The r quantum numbers $n_1 \dots n_r$ are then those on which the energy depends $E(n_1 \dots n_r)$ and are thereby the so-called principal quantum numbers.²

The expansion of $x(t)$ in terms of the w_i can be written as²

$$x(t) = \sum_m x_m \exp \left(\sum_{i=1}^N 2\pi i m_i w_i \right), \quad (2.7)$$

where x_m denotes $x_{m_1 \dots m_N}$, and the m_i 's are integers. x_m depends on $(J_1, \dots, J_N)$. Since $x(t)$ is real one has

$$x_m = x_{-m}^*. \quad (2.8)$$

For the quasiperiodic case, looking at a particular molecule, we select as the ensemble a microcanonical ensemble with fixed action variables J_i but averaged over the phases φ_i . Semiclassically, this ensemble corresponds to the molecule being in a specified quantum state. Introducing Eq. (2.7) into (2.1) or (2.5) and performing this phase average in $\langle \rangle$ (each φ_i is uniformly distributed in the unit interval) one obtains Eq. (2.9)¹⁷ for any given value of the action variables J_i ,

$$I(\omega) = \sum_m |x_m|^2 \delta \left[\left(\sum_{i=1}^r m_i \omega_i \right) - \omega \right]. \quad (2.9)$$

Thus, the spectrum in the quasiperiodic regime is a line spectrum. The m_i 's in $x_{m_1 \dots m_N}$ from $N - r + 1$ to N yield the same values of $(\sum_{i=1}^r m_i \omega_i) - \omega$, but different values of x_m .

Equation (2.5) is particularly convenient, since one finds by introducing Eq. (2.7) and performing the integration that in the quasiperiodic case the quantity inside the $\langle \rangle$ is independent of the initial phases φ_i in the microcanonical ensemble [unlike the term inside $\langle \rangle$ in Eq. (2.2)]. Thus, in the ensemble average $\langle \rangle$ no average over initial φ_i 's is needed when (2.5) is used. One then obtains Eq. (2.9), using a single trajectory. To obtain $I(\omega)$ for a Boltzmann population, one would average the expression (2.9) over a Boltzmann population of J_i 's, in which the energy in the Boltzmann factor is

written as a function of the J_i 's.

In the ergodic regime the integral in Eq. (2.5) is independent of the initial condition at a given energy for the molecule and at a given total angular momentum and z component. Thus, for this microcanonical ensemble the $\langle \rangle$ can be omitted, and a single trajectory again suffices to evaluate the integral.

In summary, the $\langle \rangle$ in Eq. (2.5) can be removed in both the ergodic and quasiperiodic cases. In this respect Eq. (2.5) has an advantage over (2.1): The $\langle \rangle$ in $C(t)$ in Eq. (2.1) in the quasiperiodic case must be computed by averaging over all φ_i there.

We have already noted that the spectrum $I(\omega)$ is a line spectrum in the quasiperiodic case. In the ergodic case the $C(t)$ in Eq. (2.1) may have both an oscillatory dependence on t and a time-decay factor or more complicated oscillatory dependence, leading thereby to broadened lines instead of sharp ones.

It is more useful to consider instead of Eq. (2.5) an integral, which we shall also label $I(\omega)$,

$$I(\omega) = \frac{1}{2\pi} \lim_{T \rightarrow \infty} \frac{1}{2T} \left\langle \left| \int_0^{2T} x(t) \exp(-i\omega t) dt \right|^2 \right\rangle, \quad (2.10)$$

since we wish to begin the trajectories and integrate forward in time. For an ergodic system this integral is clearly equal to that in Eq. (2.5). For quasiperiodic systems we introduce Eq. (2.7) for $x(t)$ and integrate over t . One obtains a sum over a product of δ -like functions of the arguments $\sum_i m_i \omega_i - \omega$ inside the absolute value signs. Any cross terms of different $\sum m_i \omega_i - \omega$ vanish for that reason. There remains

$$I(\omega) = \frac{1}{\pi} \lim_{T \rightarrow \infty} \sum_m |x_m|^2 (\sin^2 \psi_m T) / T \psi_m^2, \quad (2.11)$$

where

$$\psi_m = \left(\sum_{i=1}^r m_i \omega_i \right) - \omega. \quad (2.12)$$

Since^{17(a)}

$$\delta(x) = \frac{1}{\pi} \lim_{L \rightarrow \infty} \left(\frac{\sin^2 Lx}{Lx^2} \right), \quad (2.13)$$

one concludes that

$$I(\omega) = \sum_m |x_m|^2 \delta \left[\left(\sum_{i=1}^r m_i \omega_i \right) - \omega \right]. \quad (2.14)$$

This result is identical with Eq. (2.9), and so Eq. (2.10) is indeed equivalent to (2.5) for quasiperiodic systems (as well as for ergodic ones). We shall employ it here.

One also notes from Eq. (2.11) that the "width" of a line in the quasiperiodic regime $\Delta\omega$ varies inversely with the trajectory time $2T$.

III. NUMERICAL CALCULATIONS, RESULTS, AND DISCUSSION

Two Hamiltonians are used in the present paper for purposes of comparing the quantum mechanical spectrum with the present semiclassical one (semiclassical because of the nature of choosing the action variables).

TABLE I. Spectral lines for the Hamiltonian (3.1).^a

Parameters: $\omega_x^0=0.7$, $\omega_y^0=1.3$, $\lambda=-0.1$, $\eta=0.1$						
Initial state (n_x, n_y)	Quantum ^b		Semiclassical ^{c,d} Eq. (3.6)		Semiclassical ^d Eq. (3.7)	
	ω_x	ω_y	ω_x	ω_y	ω_x	ω_y
0,0	0.691	1.283	0.693	1.284	0.695	1.289
1,0	0.688	1.271	0.688	1.273	0.690	1.278
0,1	0.680	1.270	0.680	1.271	0.680	1.278
2,0	0.685	1.260	0.683	1.261	0.685	1.268
1,1	0.676	1.258	0.678	1.256	0.680	1.263
3,0	0.681	1.247	0.680	1.245	0.680	1.253
0,2	0.668	1.256	0.668	1.256	0.670	1.263
2,1	0.672	1.245	0.673	1.245	0.675	1.253
4,0	0.677	1.234	0.678	1.233	0.680	1.243
1,2	0.664	1.243	0.663	1.240	0.665	1.248
3,1	0.668	1.232	0.668	1.230	0.670	1.237
5,0	0.673	1.221	•	•	0.675	1.227
0,3	0.655	1.242	•	•	0.660	1.248
2,2	0.659	1.230	0.657	1.227	0.660	1.237
4,1	0.664	1.218	•	•	0.665	1.222
1,3	0.650	1.228	0.647	•	0.649	1.232
3,2	0.654	1.216	•	•	0.654	1.222
0,4	0.642	1.227	•	•	0.644	1.232
2,3	0.645	1.213	•	•	0.644	1.217

^aThe unperturbed values for these spectral lines are ω_x^0 and ω_y^0 .

^bThe first entry denotes $E(n_x+1, n_y) - E(n_x, n_y)$ and the second denotes $E(n_x, n_y+1) - E(n_x, n_y)$, for the (n_x, n_y) given in the first column, and are identified as ω_x and ω_y . A basis set of 225 harmonic oscillator wave functions (15x times 15y functions) was used.

^cThe value for (n_x, n_y) for an $\omega = \omega_x$ frequency in this column is the mean of that ω_x in the entries for (n_x, n_y) and (n_x+1, n_y) in the last column, e.g., for the (0,0) state, 0.693 (≈ 0.6925) is the mean of 0.695 and 0.690. 1.284 (≈ 1.2835) is the mean of the 1.289 and of the 1.278 appearing in the third row.

^dUncertainty in these figures is ± 0.003 .

^eIn this space and all other blank spaces sufficient data for interpolation from the Eq. (3.7) column was not available, although can readily be obtained.

One Hamiltonian is the Henon-Heiles one employed in the previous semiclassical studies^{4,5}

$$H = \frac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda(xy^2 + \eta x^3). \quad (3.1)$$

The second Hamiltonian is one with three coordinates

$$H = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2 + \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) + \lambda(xy^2 + \eta x^3) + \lambda(yz^2 + \eta y^3). \quad (3.2)$$

Hamilton's equations of motion, obtained from these Hamiltonians, were integrated with the standard integration routines,¹⁸ and a fast Fourier transform was used.^{19,19} The following semiclassical argument was used to select the initial conditions for the trajectory and to compare with the quantum results.

The action variables J_i are related to the quantum numbers n_i , in units of $\hbar = 1$, by

$$J_i = 2\pi(n_i + \frac{1}{2}) \quad (3.3)$$

for nondegenerate vibrational systems. A spectral frequency $\omega_{n'n}$ can be defined quantum mechanically by subtracting the energy E for the state with initial quantum numbers $n_1 \dots n_N$ from that for the state with the final ones $n'_1 \dots n'_N$:

$$\omega_{n'n} = E(n'_1, \dots, n'_N) - E(n_1, \dots, n_N) \cong \sum_{i=1}^N (\partial E / \partial n_i)(n'_i - n_i), \quad (3.4)$$

where the partial derivative is computed at mean values $\bar{n}_i$ of n_i and n'_i :

$$\bar{n}_i = \frac{1}{2}(n_i + n'_i), \quad i = 1, \dots, N. \quad (3.5)$$

Since $\partial E / \partial J_i$ is the usual classical mechanical frequency² ν_i , the $\partial E / \partial n_i$ in Eq. (3.4) is the usual classical mechanical angular frequency $\omega_i (= 2\pi\nu_i)$ [evaluated at $(\bar{n}_1, \dots, \bar{n}_N)$].

Thus, using the approximation contained in Eqs. (3.4) and (3.5) one calculates the frequency for a transition $(n_1, \dots, n_N) \rightarrow (n'_1, \dots, n'_N)$ using a trajectory evaluated at action variables

$$J_i = 2\pi(\bar{n}_i + \frac{1}{2}), \quad \bar{n}_i = (n_i + n'_i)/2. \quad (3.6)$$

The 1/2 in the J_i expression is for the case of nondegenerate vibrational degrees of freedom.

The initial conditions were chosen by selecting the J_i in Eq. (3.6) using the unperturbed Hamiltonian, a procedure which is sufficiently accurate since the frequencies vary only slowly with J_i , as seen later in Table I.

TABLE II. Spectral lines for the Hamiltonian (3.2).^a

Parameters $\omega_x^0=0.7$, $\omega_y^0=1.2$, $\omega_z^0=1.0$, $\lambda=-0.1$, $\eta=0.1$											
Initial state (n_x, n_y, n_z)	Quantum ^b			Semiclassical ^{c,d} Eq. (3.6)			Semiclassical ^d Eq. (3.7)				
	ω_x	ω_y	ω_z	ω_x	ω_y	ω_z	ω_x	ω_y	ω_z		
0 0 0	0.690	1.173	0.990	0.692	1.175	0.990	0.693	1.184	0.992		
1 0 0	0.687	1.159	0.990	0.688	1.161	0.990	0.690	1.169	0.992		
0 0 1	0.690	1.164	0.985	0.691	1.166	0.985	0.693	1.174	0.987		
0 1 0	0.676	1.151	0.981	0.678	1.159	0.978	0.680	1.166	0.984		
2 0 0	0.683	1.144	0.948	•	•	•	0.685	1.156	0.992		
1 0 1	0.645	1.149	0.984	•	•	•	0.688	1.161	0.987		
1 1 0	0.672	1.134	0.979	•	•	•	0.675	1.153	0.984		
0 0 2	0.689	1.153	0.979	•	•	•	0.690	1.163	0.982		
0 1 1	•	•	•	•	•	•	0.680	1.158	0.979		
0 2 0	•	•	•	•	•	•	0.665	1.151	0.977		

^aSee footnotes for Table I, apart from the fact that for the quantum entries a basis set of 512 harmonic oscillator wavefunctions was used (8x times 8y times 8z functions).

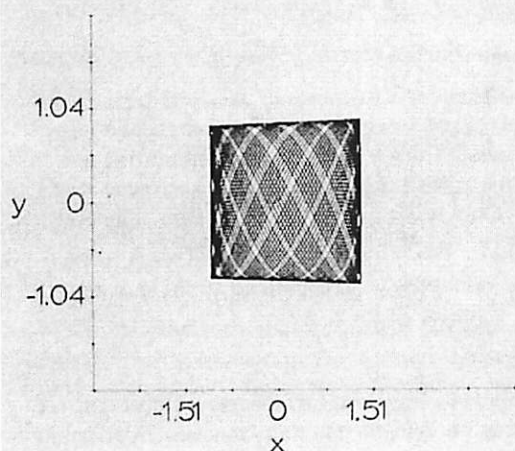


FIG. 1. A trajectory for the two-dimensional system in Table I, at total energy $E = 1.0$.

To obtain a first approximation to the frequencies one can replace the n'_i in Eq. (3.6) by n_i , yielding the result

$$J_i = 2\pi(\bar{n}_i + \frac{1}{2}), \quad \bar{n}_i \approx n_i. \quad (3.7)$$

By utilizing results based on Eq. (3.7) interpolatively as described later, one can obtain an answer based on Eq. (3.6) or one can use (3.6) directly. The procedure via Eq. (3.7) uses fewer trajectories than one based directly on Eq. (3.6), in obtaining an array of frequencies involving fundamentals, overtones, and combinations.

When the frequencies are well separated, the computation of the spectrum of a single function $x(t) + y(t)$ in the two-dimensional case or of $x(t) + y(t) + z(t)$ in the 3D case suffices to determine the frequencies. Otherwise, it is best to obtain spectra of $x(t)$, $y(t)$ separately.

The results are tabulated for two-dimensional and three-dimensional systems in Tables I and II. A typical trajectory, its correlation function, and its spectrum are given in Figs. 1–3 for a quasiperiodic two-dimensional case. In Fig. 4 the spectrum of a quasiperiodic three-dimensional system is shown, and in Fig.

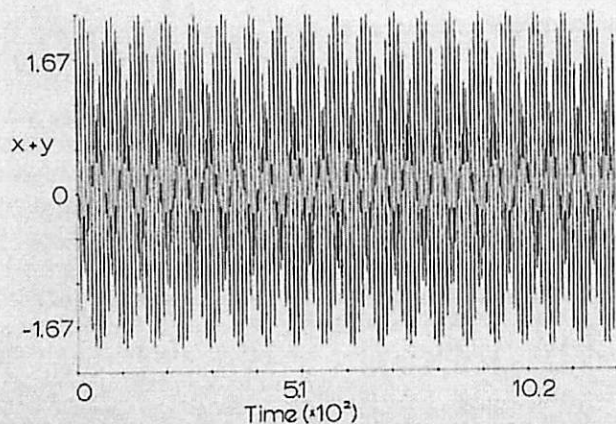


FIG. 2. The function $x(t) + y(t)$ versus t for the trajectory in Fig. 1. The fundamentals and some overtones and combinations are observed.

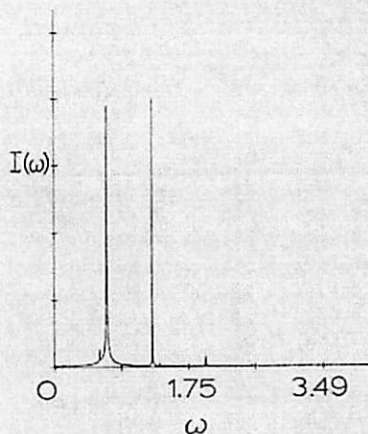


FIG. 3. Spectrum for the function $x(t) + y(t)$ using the trajectory in Fig. 1 and computed from Eq. (2.10).

5 is given a spectrum for an ergodic three-dimensional case. The extra broadening in Fig. 5 is quite evident. The spectrum in Fig. 5 refers to a system where Benettin *et al.*²⁰ applied a stochastic parameter test,²¹ and predicted that the system would be ergodic under the conditions used for Fig. 5. The ergodicity manifested in the spectrum in Fig. 5 is thus in agreement with this prediction. The trajectory itself tended to fill the energetically available configuration space.

The first semiclassical column in Tables I and II was obtained from the last by a linear interpolation: The (n_x, n_y) quantum entry in Table I refers to a $(n_x, n_y) - (n_x + 1, n_y)$ transition. The last semiclassical column is based on Eq. (3.7) and contains an $\omega = \omega_x$ for an (n_x, n_y) state. To obtain a result for (n_x, n_y) but based on Eq. (3.6) we used the arithmetic mean of the ω_x spectral frequencies in the Eq. (3.7) column for the (n_x, n_y) and $(n_x + 1, n_y)$ entries.

The agreement of Eq. (3.6) with the quantum results is seen to be excellent in Tables I and II.

The spectral analysis method could also be used to generate the frequencies for molecular spectra not only in the anharmonic regime, as above, but also to generate the normal mode frequencies associated with any force field in a straightforward manner, merely by using small initial amplitudes.

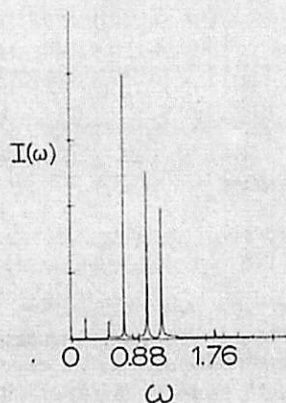


FIG. 4. Spectrum for the function $x(t) + y(t) + z(t)$ for the three-dimensional system in Table II, at a total energy $E = 1.45$.

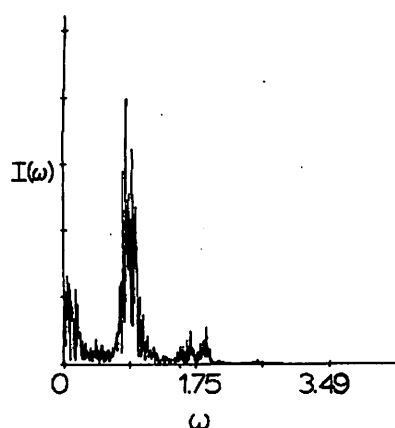


FIG. 5. Spectrum for a two-dimensional system with the Hamiltonian (3.1) and $\omega_x^0 = \omega_y^0 = 1$, $\lambda = 0.1118$, $\eta = -1/3$, $E = 11.0$.

The present method is much faster than previous semiclassical methods^{4,5}. It does not involve a multi-dimensional search for a trajectory to satisfy the semiclassical quantum conditions. Applications to actual molecules are in progress, and to systems which are degenerate in zeroth order. In the 1:1 nearly degenerate case power spectra of quantities such as r and p_r are simpler to interpret than those of x and y , and are being used here. The methods developed in Refs. 4 and 5 would be superior, when extended to include tunneling, for states having tunneling, e.g., in certain two-well problems.

The observation that the spectrum is centered on certain frequencies, in the ergodic regime, supports the assumption normally made in unimolecular reaction theory that the high energy molecule can be described in terms of certain frequencies even though the usual normal modes exist only in some average sense at most.

ACKNOWLEDGMENTS

We are pleased to acknowledge support of the present research by a grant from the National Science Foundation and by the award of a University of Illinois Fellowship (M. L. K.).

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¹³Reference 12, Eq. (10-3).

¹⁴Reference 12, pp. 338, 343-344.

¹⁵Reference 12, p. 343.

¹⁶In Ref. 12, p. 344, it is shown that the right hand side of Eq. (2.5) equals the right hand side of (2.1) minus a term:

$$\lim_{T \rightarrow \infty} \frac{1}{2T} \int_{-T}^T |t| C(t) \exp(-i\omega t) dt.$$

Introduction of Eqs. (2.2), (2.6) and (2.7) and use of the δ function in Ref. 17(b) reveals an exact vanishing of this term for the quasiperiodic case.

¹⁷(a) In the derivation leading from Eqs. (2.5) to (2.9) we use the fact that $\int_{-\infty}^{\infty} (\sin^2 Lx)/(Lx^2) dx = \pi$, and that as $L \rightarrow \infty$ the integrand becomes increasingly peaked at $x=0$ [cf. I. M. Ryshik and I. S. Gradshteyn, *Tables of Series, Products, and Integrals* (Deutscher Verlag, Berlin, 1963)], p. 166. That is, $\delta(x) = \lim_{L \rightarrow \infty} (\sin^2 Lx)/\pi Lx^2$; (b) In the derivation leading from Eq. (2.1) use is made of the fact that $\lim_{L \rightarrow \infty} \sin Lx/\pi x = \delta(x)$.

¹⁸All programs were executed using Fortran and an IBM 360-75 computer. DHPCG was used for the two-dimensional systems and DE (a new program available from Argonne National Laboratory) was used for the three-dimensional system. The trajectory length for the 2D problems was 1400 time units, and the functions $x(t)$ and $y(t)$ were computed every 0.3 time units. The fast Fourier cosine and sine transform was calculated with an IMSL program FFCOSIN, and the spectra are the sum of the squares of the sine and cosine transforms. The frequencies were checked using the programs with $\lambda = \eta = 0$ in Eq. (3.1). The spectra gave $\omega_x^0 = 0.7005$ and $\omega_y^0 = 1.299$, in excellent agreement with the exact values of 0.7000 and 1.3000, respectively; 4096 points were used for these transforms, though 2048 points sufficed.

¹⁹In a Fourier series package one uses a discrete set of points $x(t_i)$, corresponding to various times t_i along the trajectory. This step amounts to a multiplication of $x(t)$ by a sum of step functions of unit height and zero width, centered at the t_i 's, and produces an intrinsic limit to the spectral resolution.

²⁰G. Benettin, L. Galgani, and J. Strettin, Phys. Rev. A 14, 2338 (1976).

²¹See M. Casartelli, E. Diana, L. Galgani, and A. Scotti, Phys. Rev. A 13, 1921 (1976) for references to the literature.