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INTRAMOLECULAR DYNAMICS IN THE QUASIPERIODIC AND STOCHASTIC REGIMES*

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

Oak Ridge National Laboratory, Oak Ridge, TN 37830
Sandia National Laboratories, Livermore, CA 94550
California Institute of Technology, Pasadena, CA 91125

INTRODUCTION

Nonlinear dynamics has been the subject of intense study in recent years. In this review article, we present a summary of our recent work in this field, in which nonlinear dynamics is applied to problems involving molecular behavior. Four aspects are described: (1) semiclassical methods for the calculation of bound-state eigenvalues, (2) classical spectra and correlation functions in the quasiperiodic and "chaotic" regimes, (3) "chaotic" behavior in quantum mechanics, and (4) applications to collisional and laser interactions.

I. SEMICLASSICAL METHODS FOR THE CALCULATION OF BOUND-STATE EIGENVALUES

The calculation of bound-state properties using semiclassical concepts has been of interest for many years.[1-3] This problem has a well-known WKB solution for systems permitting separation of variables. Recently, several methods of calculating eigenvalues for non-separable systems that are quasiperiodic have been presented. The earliest method[4] for systems with smooth potentials involves the use of classical trajectories for the calculation of the phase space path integrals ("actions") used to quantize the system and hence find the semiclassical eigenvalues.

The studies involved systems with incommensurate frequencies[4a-4c]

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and then systems with a 1:1 zeroth order commensurability.[4d] Recently we have been able to extend the applicability of this method to systems that have Fermi resonance[4e] and to systems with more degrees of freedom.[4f] The system that exhibits Fermi resonance has frequencies of the unperturbed problem in a ratio of 1:2 and also a perturbation term that couples the two degrees of freedom resonantly. The Hamiltonian which we used in this calculation is

$$H = \frac{1}{2}(p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda(xy^2 - \beta x^3) \quad . \qquad \text{(I-1)}$$

A typical trajectory of Hamiltonian (1) is shown in Fig. 1. Introducing a curvilinear Poincaré surface of section (in parabolic coordinates), we were able to calculate the eigenvalues semiclassically.

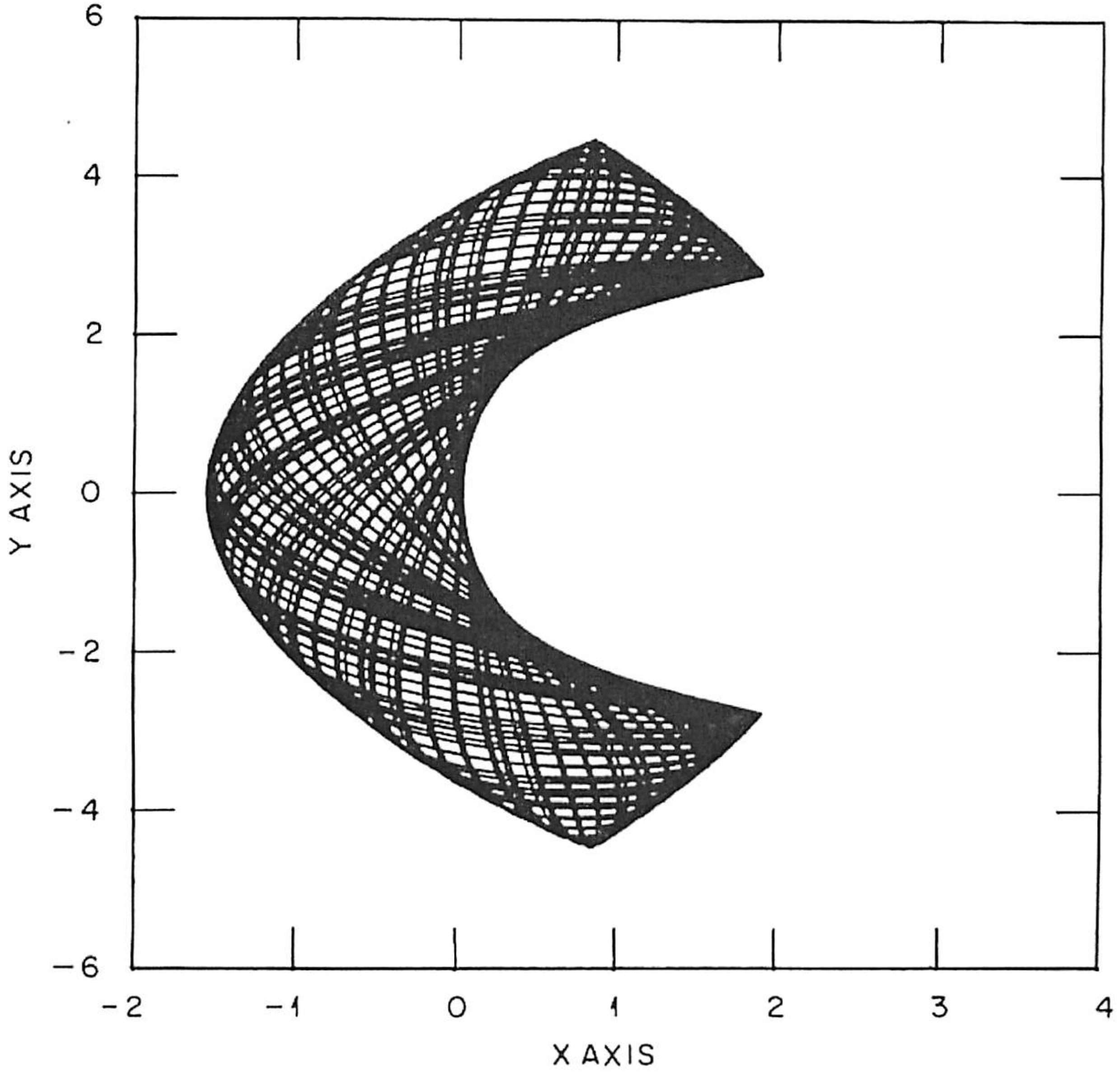

Fig. 1. A quasiperiodic trajectory for Hamiltonian (I-1) which has a Fermi resonance.

The path used in our calculation is shown in Fig. 2 (ξ and η are parabolic coordinates). An example of a p_ξ vs. ξ Poincaré surface of section for η = constant is shown in Fig. 3. The quantum conditions for this type of trajectory were ($\hbar = 1$)

$$J_\xi = \oint p_\xi d\xi = 2\pi(n_1 + \tfrac{1}{2}) \tag{I-2a}$$

and

$$J_\eta = \oint p_\eta d\eta = 2\pi(n_2 + \tfrac{1}{2}) \ . \tag{I-2b}$$

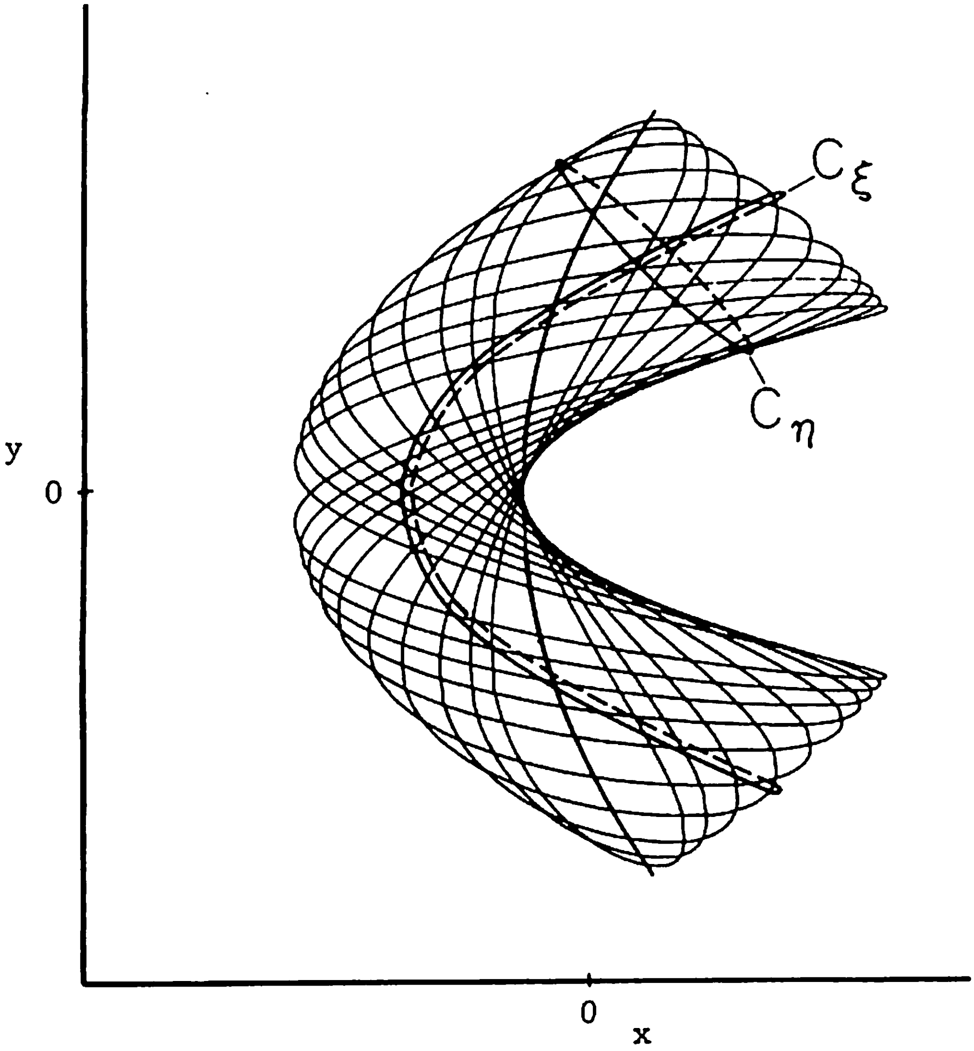

Fig. 2. Path used for quantization of the trajectory in Fig. 1.

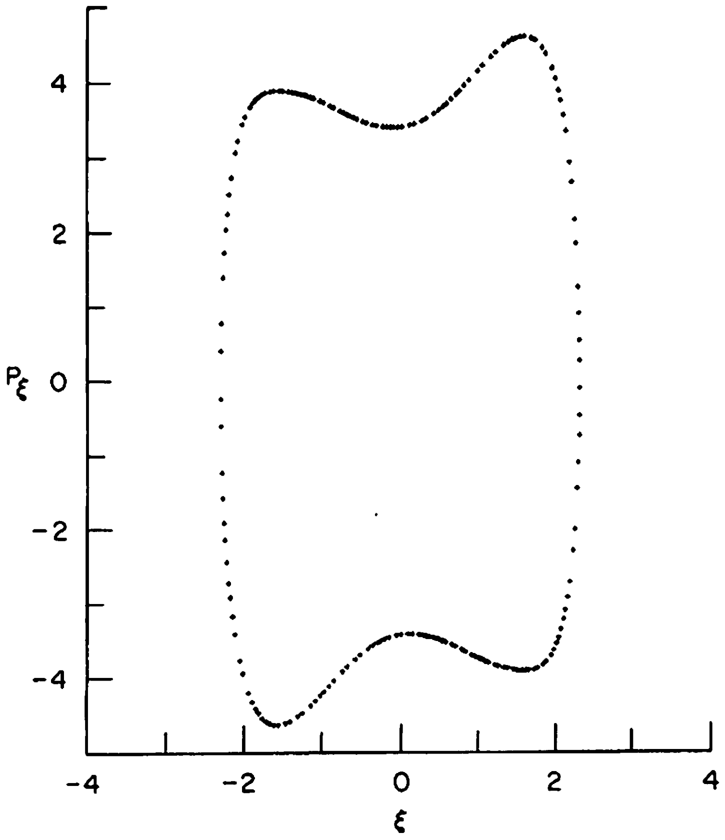

Fig. 3. An example of a P_ξ, ξ surface of section (η = constant, $P_\eta \geqslant 0$).

We found usually very good agreement between quantum and semiclassical eigenvalues. Since our method depends on having quasiperiodic motion, we were not able to calculate eigenvalues for all of the bound states for this Hamiltonian. For example, at $E = 6$ in our units, the trajectories became predominantly "chaotic", as shown in Fig. 4. An interesting feature of Hamiltonian (1) is that for $\beta = -2$, the Hamiltonian-Jacobi equation is separable in parabolic coordinates and hence cannot exhibit chaotic motion. A recently developed

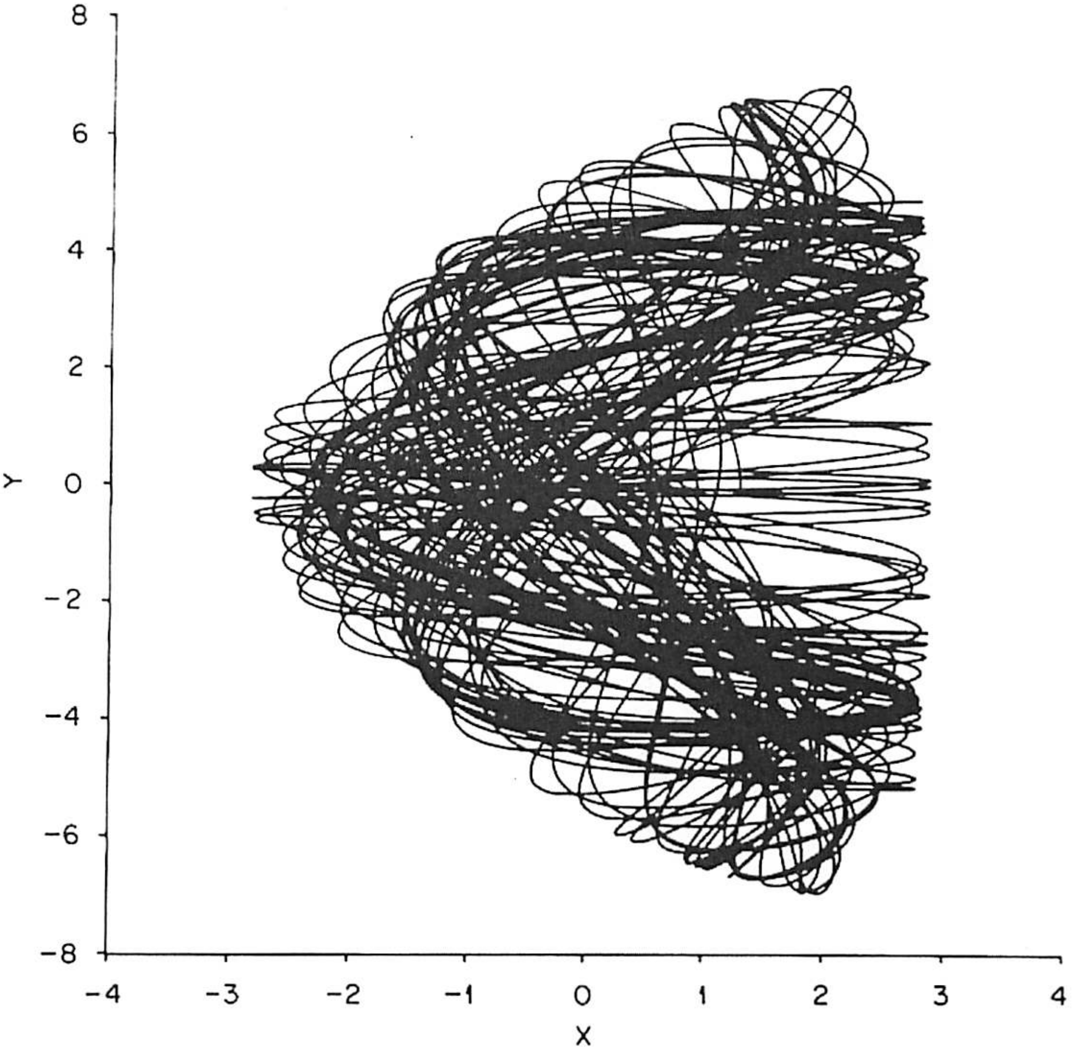

Fig. 4. A chaotic trajectory of Hamiltonian (I-1).

method[5] for the chaotic limit was applied to this model for the separable case, and it was found that for a large range of x, y initial conditions, the prediction is incorrect.[4e]

A method for calculating eigenvalues for systems with more degrees of freedom has also been developed.[4f] This method is an extension of the Poincaré surface of section method. Now, we use a surface of section in 2N-dimensional phase space, with a small but finite width in several coordinate directions. This surface of section with the appropriate path integrals is shown in Fig. 5. A surface of section calculated this way for the Hamiltonian

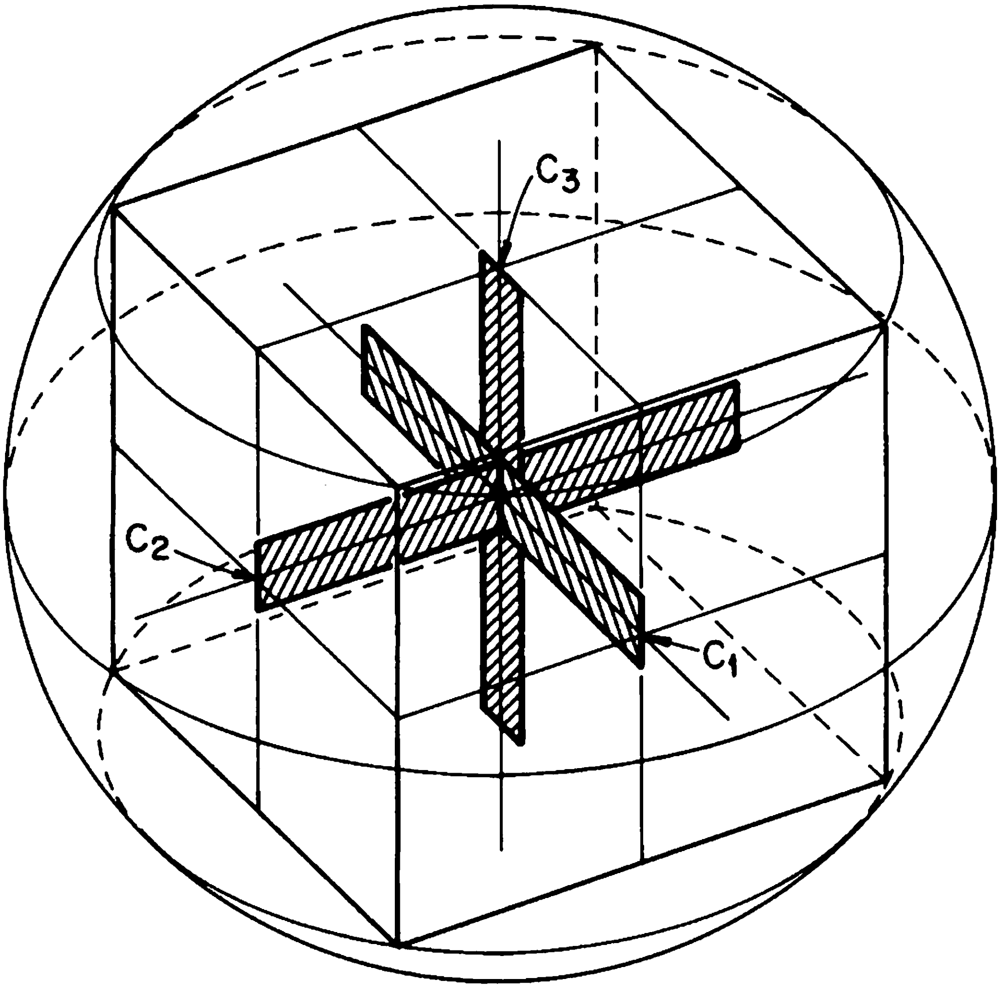

Fig. 5. Diagram showing the three paths for quantization in a system of three coupled oscillators (Hamiltonian (I-3)).

$$
\begin{aligned}
H = {} & \frac{1}{2}(p_x^2 + p_y^2 + p_z^2 + \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2) \\
& + \lambda(xy^2 - \eta x^3) + \lambda(yz^2 - \eta y^3)
\end{aligned}
\qquad \text{(I-3)}
$$

is shown in Fig. 6. Upon calculation of the three path integrals $J_x = \oint p_x dx$, $J_y = \oint p_y dy$, and $J_z = \oint p_z dz$, the values of J_i's can be interpolated for $J_i = 2\pi\ (n_i + \frac{1}{2})$, and the energy eigenvalues can be obtained. The agreement with the quantum mechanical eigenvalues was excellent.

In studies of unimolecular reaction rate theory, particularly for comparison with classical trajectory results, it is useful to have a method of calculating the number and density of states for

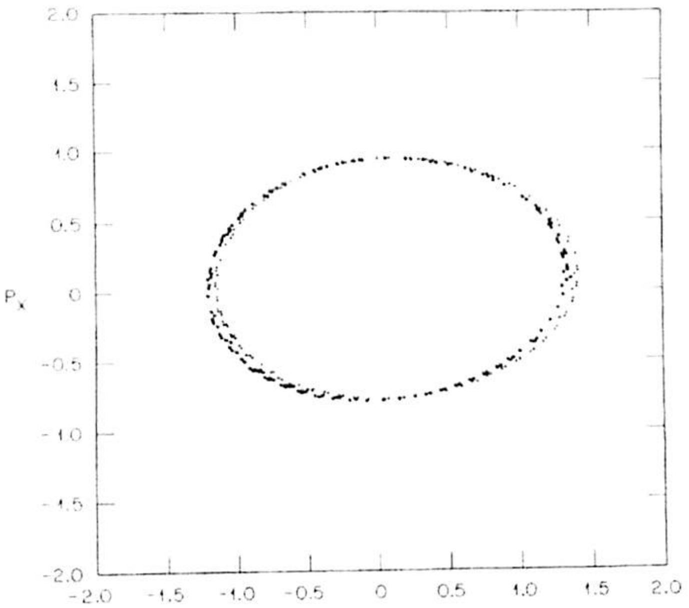

Fig. 6. A Px, x surface of section for Hamiltonian (I-3).

nonseparable systems.[6] The "classical" number of states $N_{c\ell}(E)$ for a system of n-degrees of freedom is simply given by

$$N_{c\ell}(E) = \frac{1}{(2\pi\hbar)^n} \int d\underset{\sim}{p} \int d\underset{\sim}{q}\, \theta(E-H(\underset{\sim}{p},\underset{\sim}{q})) \qquad \text{(I-4)}$$

where p and q are the n-dimensional vectors of momentum and conjugate coordinate, respectively. θ is the (unit) step-function. (The density of states is just $dN_{c\ell}(E)/dE$.) The integral can be evaluated quite rapidly using efficient Monte Carlo procedures. In Fig. 7, the smooth $N_{c\ell}(E)$ is compared with the corresponding exact quantal result for the case of a model Hamiltonian with two degrees of freedom. The agreement is very good. An analogous problem (Sinai Billiard Problem) has been recently solved by Berry[1b] with similar agreement.

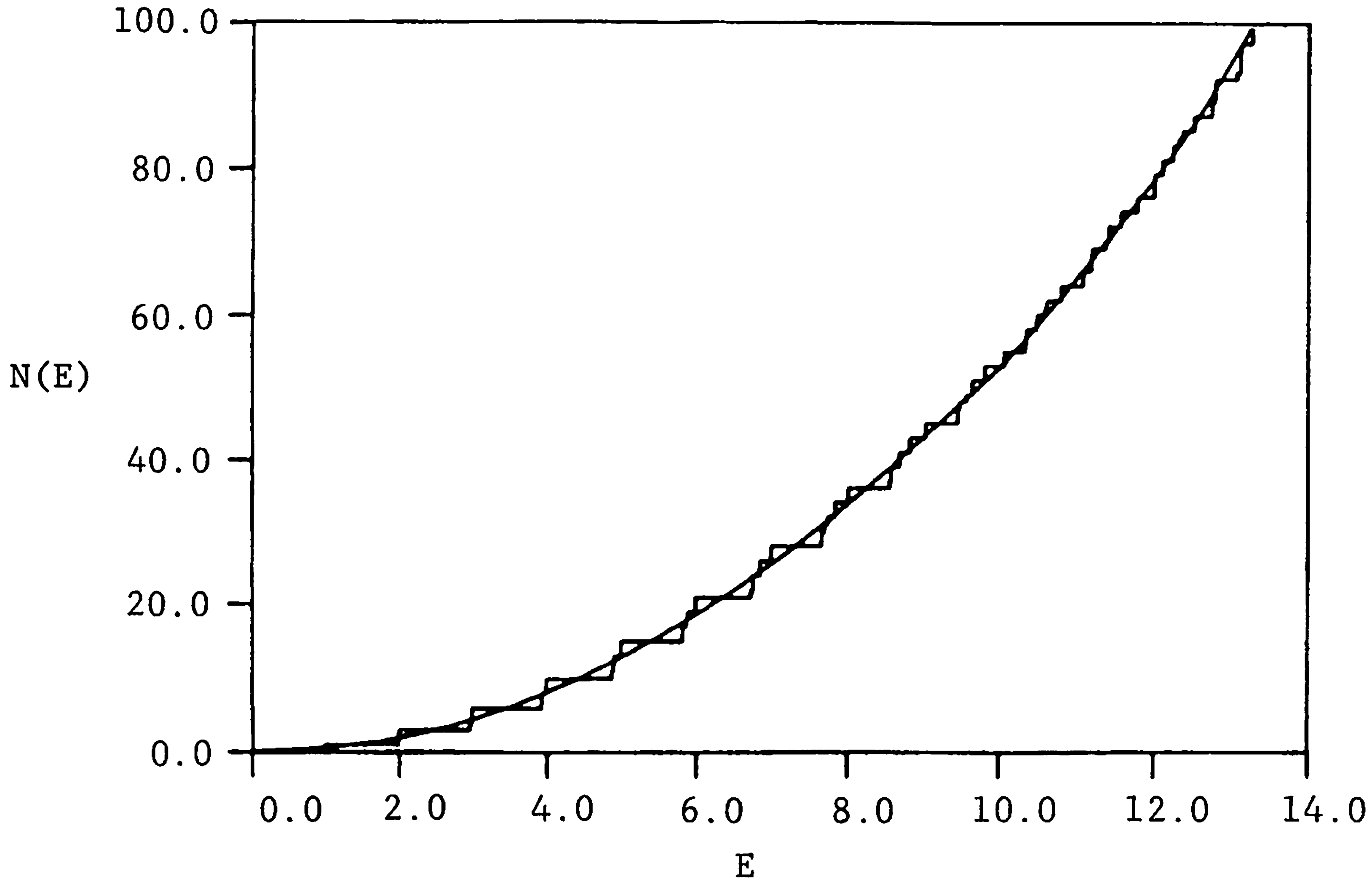

Fig. 7. A plot of the classical and quantum density of states for the Hénon-Heiles Hamiltonian.

II. SPECTRA AND CORRELATION FUNCTIONS

In the quasiperiodic regime, we have demonstrated[6,7,8] that the semiclassical (calculated from trajectories) and quantum (calculated from "exact" wavefunctions) power spectra are directly comparable in both frequency and intensity. More recently, this method of generating a spectrum from classical trajectories has also been used by Hansel[9] and Powell, et al.[10]

Briefly, we obtained the classical autocorrelation function, C(t), by averaging (e.g., the correlation eq. of the dipole) the appropriate ensemble. The classical spectrum, $I(\omega)$ is then given by the Fourier transform of the autocorrelation function

$$I(\omega) = \frac{1}{2\pi}\int_{-\infty}^{\infty}\langle\mu\cdot\mu(t)\rangle e^{i\omega t}dt \; . \qquad \text{(II-1)}$$

Recently, another spectral method has been introduced by Heller.[11]

The justification of the use of classical trajectories to obtain semiclassical spectra will be restated now. The quantum power spectrum is

$$I(\omega) = \sum_{k}|\langle k|\mu|n\rangle|^{2}\delta(\omega - \omega_{kn}) \qquad \text{(II-2)}$$

where we have assumed only state $|n\rangle$ is initially populated and $\omega_{kn} = \frac{1}{\hbar}(E_k - E_n)$, or the transition frequency. Introducing the semiclassical wavefunction

$$\langle w|n\rangle = e^{2\pi inw} \; , \qquad \text{(II-3)}$$

the matrix element for the dipole operator for quasiperiodic motion becomes

$$\langle k|\mu|n\rangle = \int_0^1 e^{-2\pi ikw}\mu(\underset{\sim}{J},\underset{\sim}{w})e^{2\pi inw}dw \; . \qquad \text{(II-4)}$$

Performing the operation gives

$$\langle k|\mu|n\rangle = \int_0^1 \mu(J_n,w)e^{2\pi i(n-k)w}dw \; , \qquad \text{(II-5)}$$

which is the $(n-k)^{th}$ Fourier component of the dipole moment μ. Introducing eq. (II-5) into eq. (II-2) results in

$$I(\omega) = \sum_{s}|\mu_s(n)|^2\;\delta(\omega - \omega_s(n)) \qquad \text{(II-6)}$$

where $\omega_s(n)$ is the classical frequency component on the torus ($\simeq\omega_{kn}$). μ_s is the Fourier coefficient for the dipole operator dependent on the action variable, J. Eq. (II-6) is exactly the result previously used.[7]

A typical quasiperiodic spectrum is shown in Fig. 8 and comparison of semiclassical and quantum frequencies for various states is given in Table 2 of Ref. 7 for a three-oscillator system. A comparison of both frequency and intensity is shown in Fig. 9 for a single Morse oscillator.[8] In Fig. 9, it is clear that not only the frequencies and intensities of the "allowed" transitions are predicted, but also those of the overtones are correctly predicted with appropriate interpolation.[8]

At higher energies, the motion becomes chaotic and the spectrum is composed of a broad distribution of sharp peaks.[6,7] A microcanonically averaged spectrum forms a broad envelope of the single trajectory spectrum and is shown in Fig. 10. There have not been definitive comparisons of semiclassical and quantal stochastic spectra,[6] and we are currently studying the comparison.

In contrast to the above correlation functions, the mode energy correlation function (i.e., $<E_n E_n(t)>$ where E is the energy in the nth normal mode) is important not to molecular spectra, but to reaction rate theory.[12] Some chemically interesting experiments involve the excitation of a given bond or mode, for example in infrared multiphoton absorption, with subsequent decay of the excitation energy into other modes.

We have numerically evaluated several different correlation functions using microcanonical averages.[12] As expected, the correlation function in the quasiperiodic regime is oscillatory and is shown in Fig. 11.

In the chaotic regime, it has been previously postulated[13] that the correlation function will behave exponentially. The correlation function in the chaotic regime has, in addition to the usual property present in all regimes given by

$$c(o) = <a \cdot a(o)> = <a^2> , \tag{II-7}$$

also the property that

$$c(\infty) = <a \cdot a> = <a><a(\infty)> = <a>^2 . \tag{II-8}$$

In general, $<a^2> \neq <a>^2$ and $c(t)$ will decay to some value. From the present system, we expect[12] $\frac{c(\infty)}{c(o)} \sim 3/4$ in the chaotic regime, which is consistent with the results shown in Fig. 12. We have modeled the

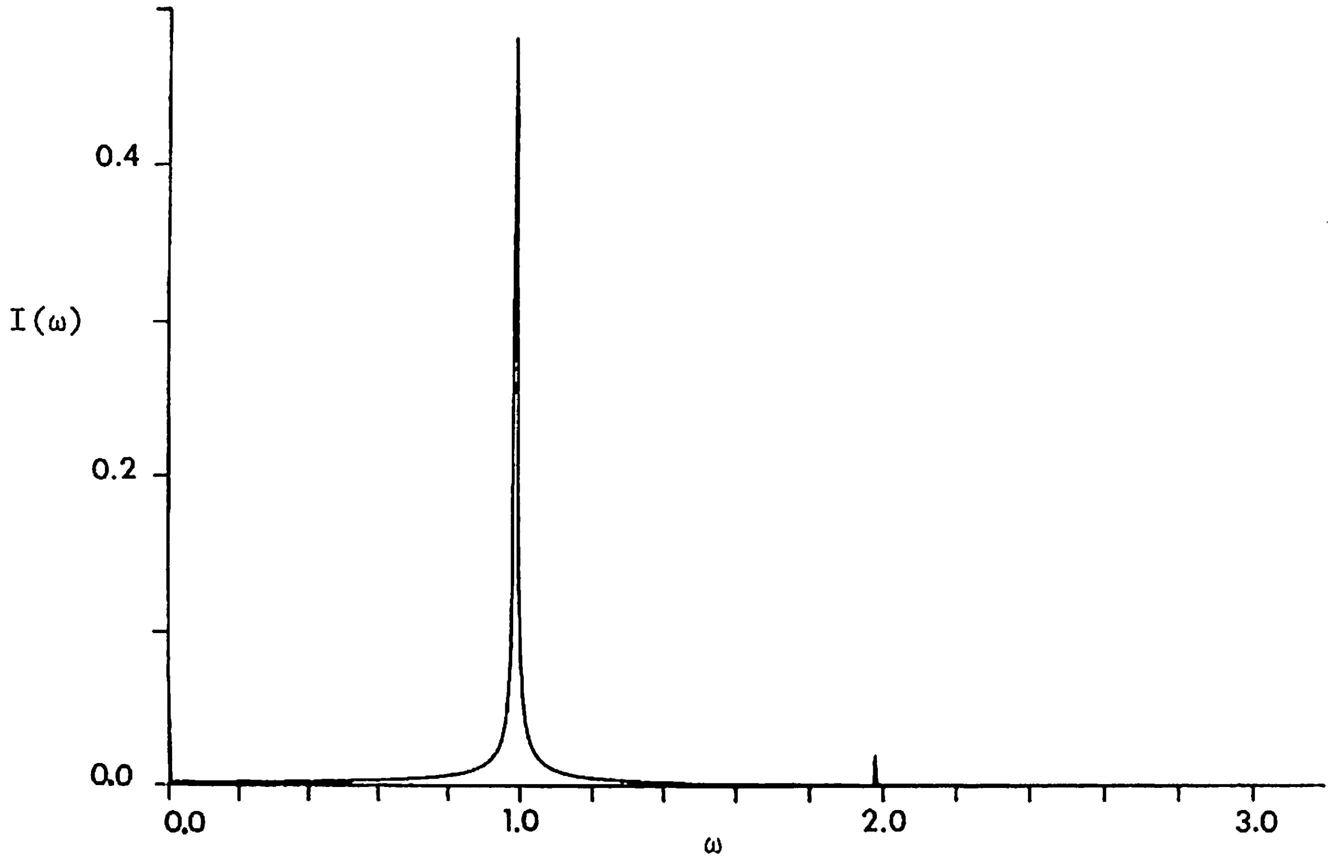

Fig. 8. A quasiperiodic spectra of a single trajectory.

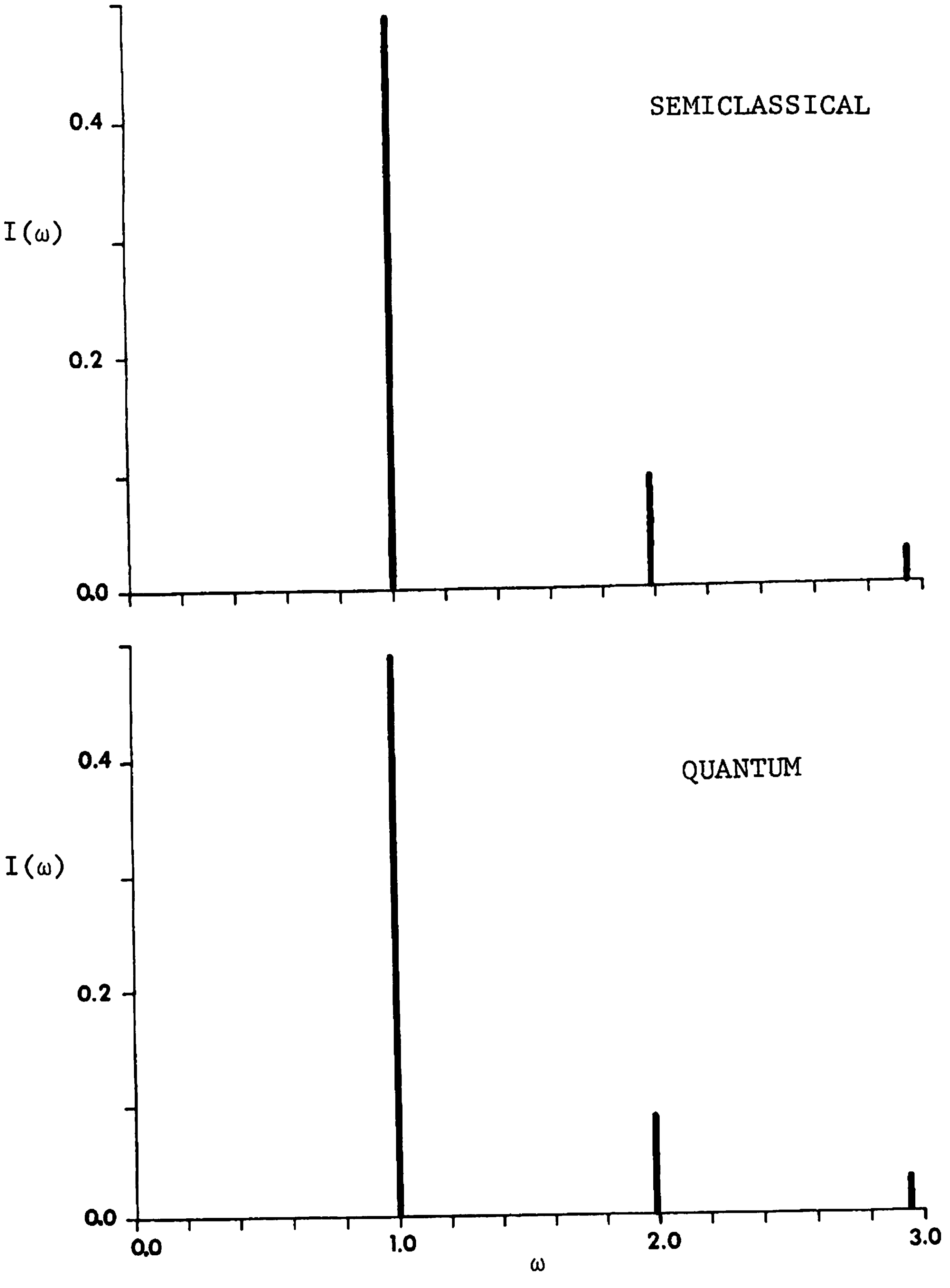

Fig. 9. Quantum and semiclassical spectrum for a Morse oscillator.

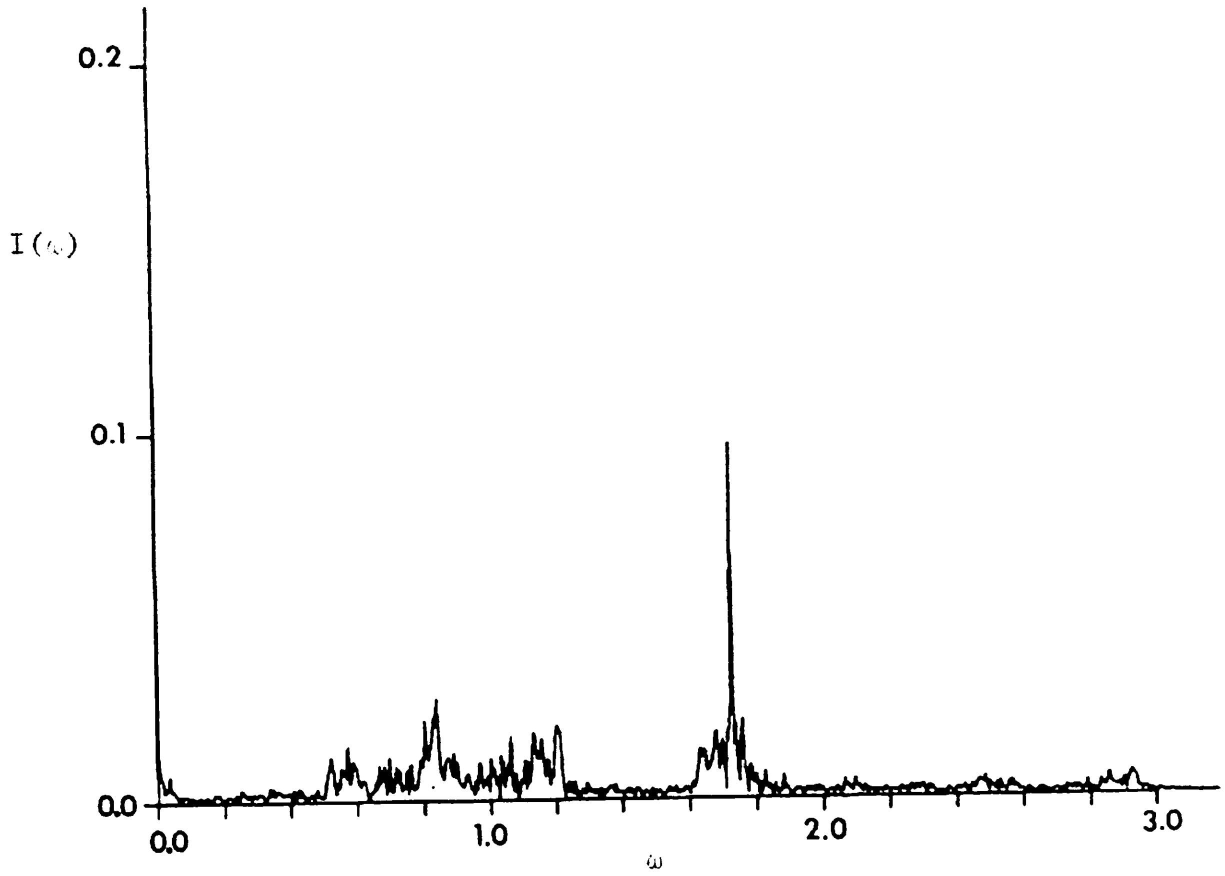

Fig. 10. As in Fig. 8, but for the chaotic regime.

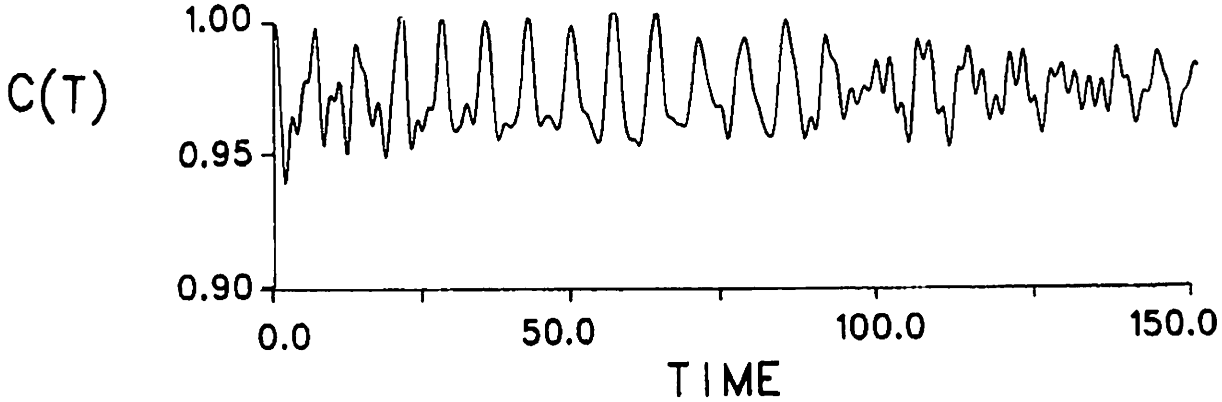

Fig. 11. Correlation function for quasiperiodic motion.

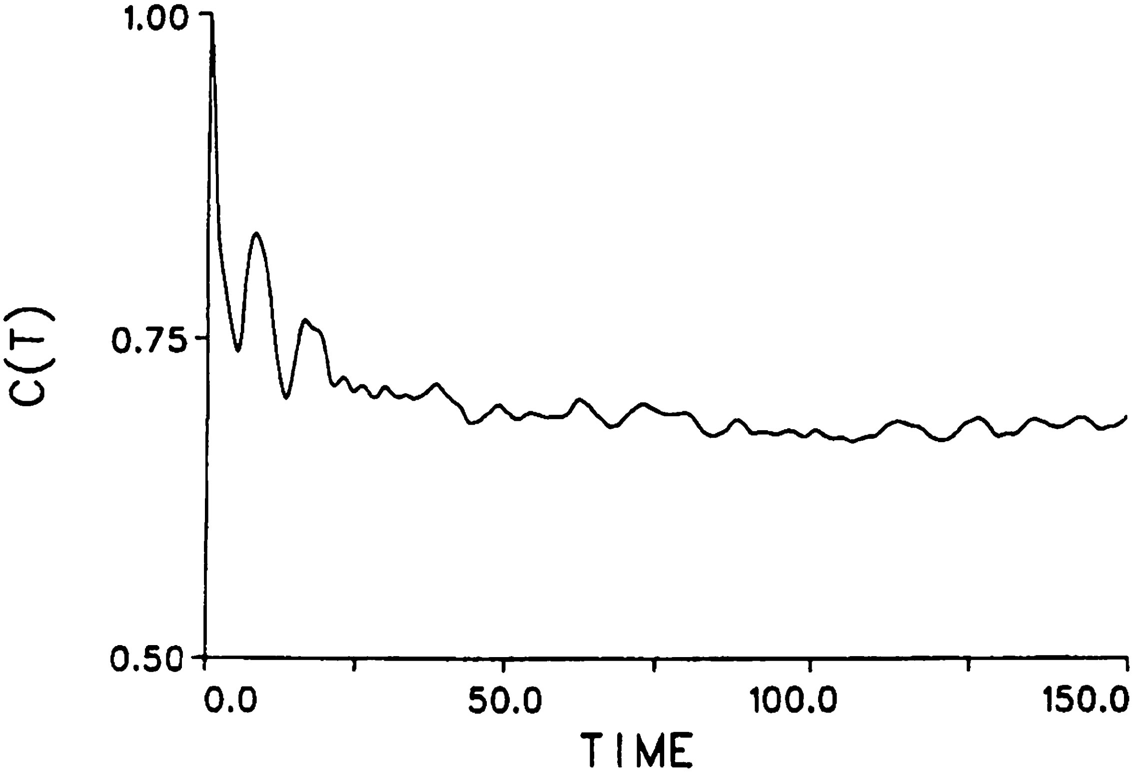

Fig. 12. Correlation function for chaotic motion.

memory functions of Figs. 11 and 12, with the result in the chaotic regime being

$$c(t) = a + (b \cos \omega_1 t + c)e^{-dt} + f \cos \omega_2 t \ , \qquad \text{(II-9)}$$

and in the quasiperiodic regime

$$c(t) = a' + b' \cos \omega_1 t + f' \cos \omega_2 t \ , \qquad \text{(II-10)}$$

with a corresponding result in the memory function.[12] The correlation functions of molecular systems are currently under investigation.[14]

III. CHAOTIC BEHAVIOR IN QUANTUM MECHANICS

The classical motion of nonlinearly coupled oscillators tends to be predominantly "quasiperiodic", or "regular", at low energies, the trajectories being confined to N-dimensional tori in phase space. At higher energies, the motion can become predominantly "chaotic" or "irregular",[15] displaying great sensitivity to small changes in in-accessible phase space. In a study of the quantum mechanical wavefunctions of a system with (2:1) Fermi resonance, we noted an analogous behavior; namely, in the quasiperiodic regime, the wavefunctions tended to be localized in well-defined regions of configuration space. On the other hand, in the chaotic regime, the wavefunctions spread over most of the allowed configuration space. The wavefunction for the trajectory in Fig. 1 is shown in Fig. 13.[4e,4g] The chaotic type wavefunction for the trajectory in Fig. 4 is shown in Fig. 14.[4e,4g]

Another well-known suggestion of quantum chaotic behavior is from Percival[16] and Pomphrey[17] and is related to the second differences. Second differences of eigenvalues were calculated from

$$\Delta^2 E_i = E_i(\lambda + \delta\lambda) - 2E(\lambda) + E_i(\lambda - \delta\lambda) \qquad \text{(III-1)}$$

using a $\delta\lambda = 0.001$. The $\Delta^2 E_i$'s are divided by E_i for normalization. The results are plotted in Fig. 15. Apart from two distinctly large values of $\Delta^2 E_i$'s not in the figure and discussed below, the second differences seem to form distinct families. The family of smaller $\Delta^2 E_i$'s tended to belong to those states with high ℓ quantum numbers (internal angular momentum like quantum numbers[4d]), whereas the family with the larger $\Delta^2 E_i$'s belong to states with low ℓ. In this study, we found that only the cases of avoided crossing or crossing of eigenvalues in the $E(\lambda)$ vs. λ plots did extremely large second differences result, and so avoided crossings provide a mechanism for the origin of such large second differences.[6]

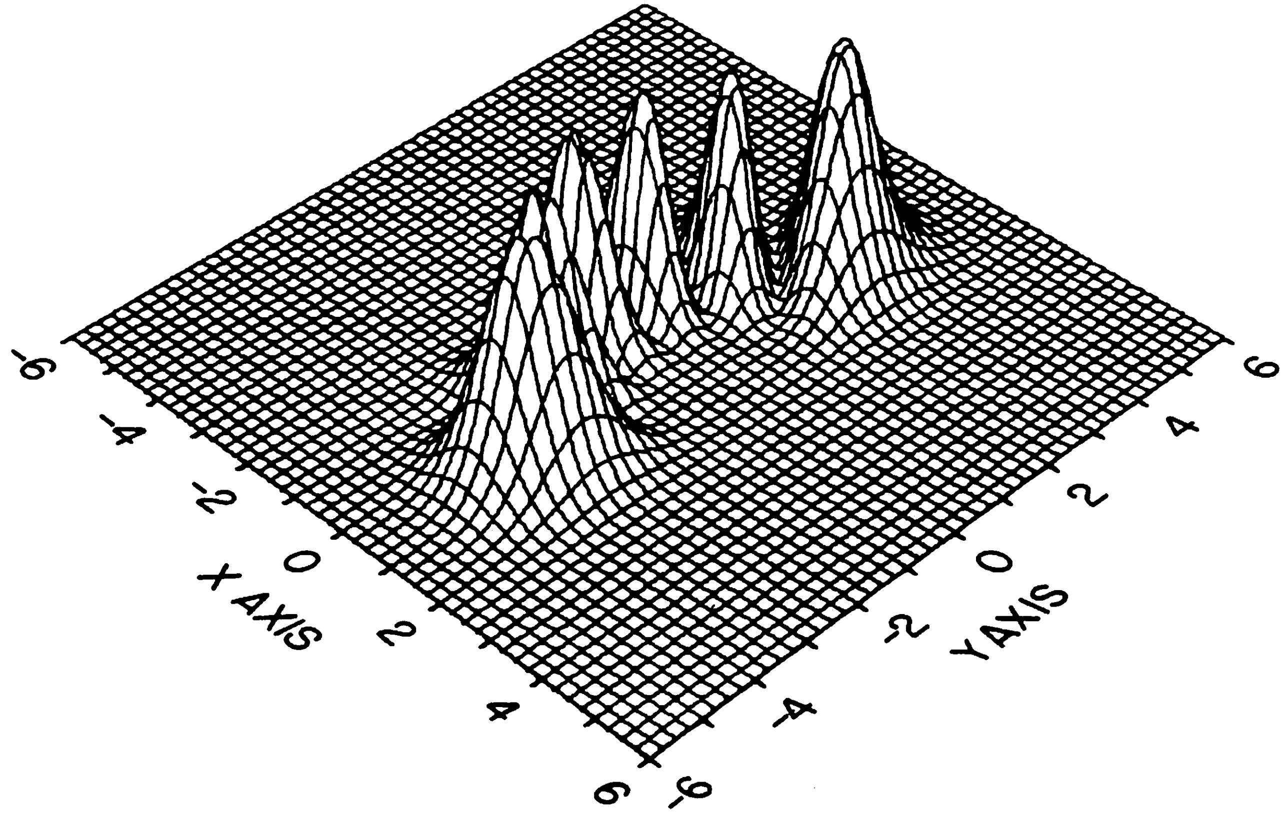

Fig. 13. Wavefunction ($\psi^*\psi$) for quasiperiodic classical motion for Hamiltonian (I-1) correponding to the trajectory in Fig. 1.

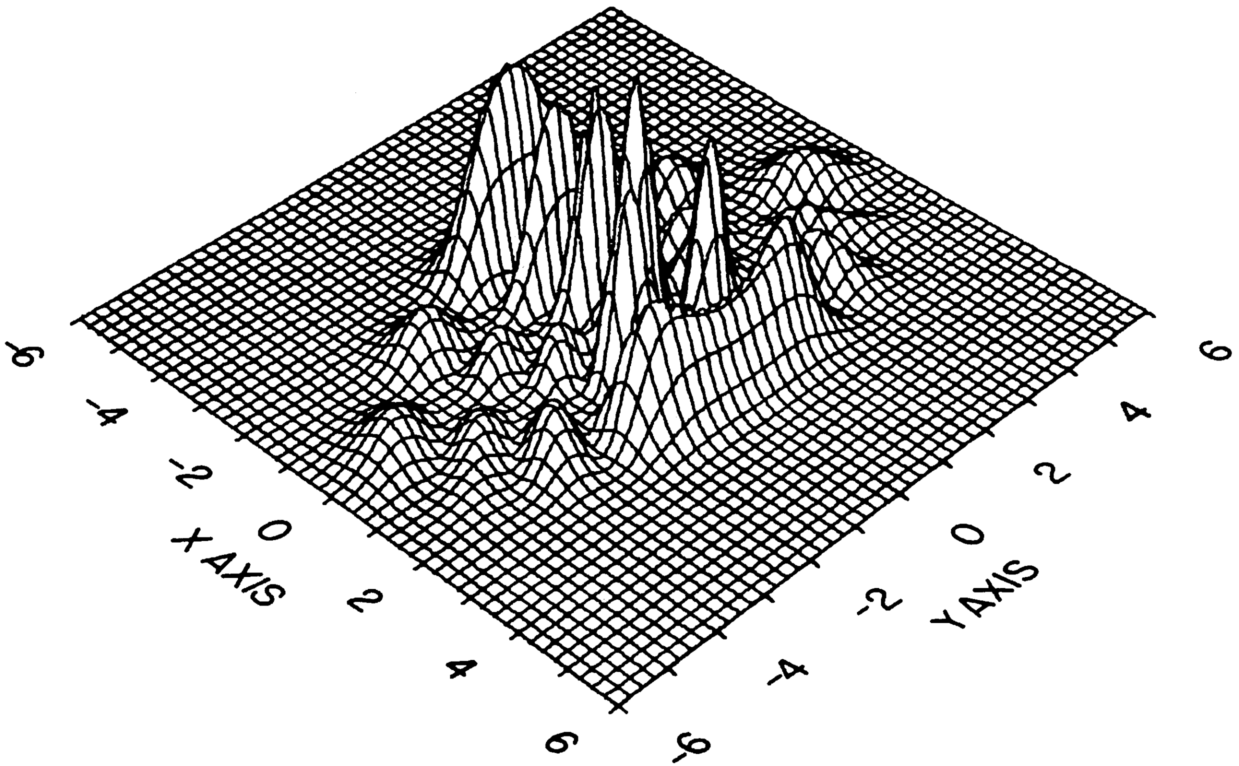

Fig. 14. Wavefunction ($\psi^*\psi$) for chaotic classical motion shown in Fig. 4 for Hamiltonian (I-1).

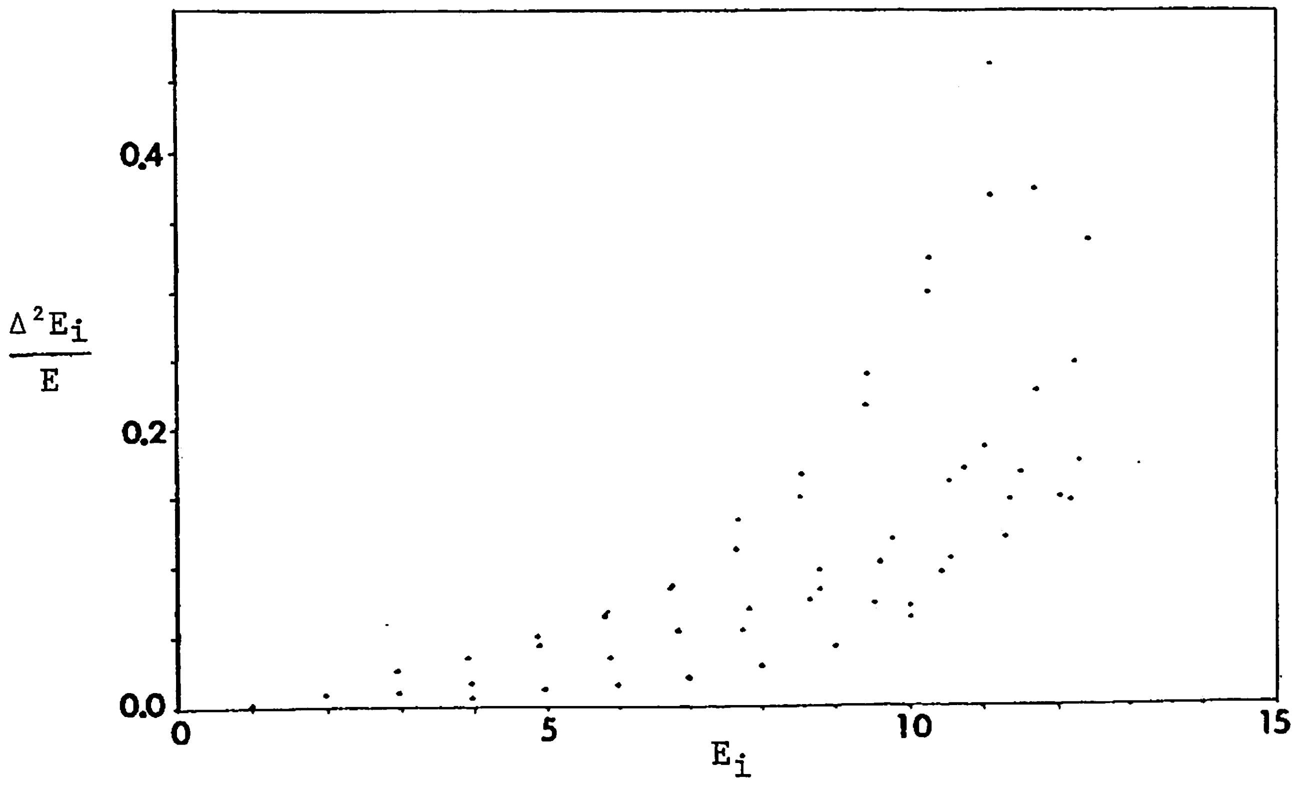

Fig. 15. A normalized plot of second differences for the Hénon-Heiles Hamiltonian.

In a recent manuscript,[18] we illustrated the avoided crossing behavior for a system of three coupled anharmonic oscillators with a Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2 + p_z^2 + \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2)$$

$$+ K_{122}xy^2 + K_{133}xz^2 + K_{233}yz^2 + K_{111}x^3 + K_{222}y^3 \qquad \text{(III-2)}$$

$$+ K_{1122}x^2y^2 + K_{2233}y^2z^2 \, .$$

In Figs. 16 and 17, the eigenvalues E are plotted versus K_{122} for two ranges of energy. In the lower range, Fig. 16, no avoided crossings are observed. Above a certain energy, there are an increasing number of overlapping avoided crossings, as in Fig. 17. These figures were drawn through points at $-K_{122} = 0.10, 0.11, \ldots, 0.16$, and hidden symmetries were assumed absent. In that case, there are no curve crossings, since curve crossings would then correspond to a conical intersection in an energy versus multidimensional parameter space, and such crossings would be of "measure zero". Overlapping avoided crossings, we have suggested,[19] will produce a statistical behavior in the wavefunctions for the quantum mechanically chaotic regime.

Finally, we would like to comment on the relation of the idea of avoided crossings to some other work in the literature related to quantum chaotic behavior, and also to provide preliminary evidence for the expectation that as $h \to 0$, overlapping avoided crossings correspond to classical chaos. We have seen that avoided crossings produce large second differences in plots of eigenvalues versus perturbation parameter. Pomphrey studied second differences for the Hénon-Heiles potential, using a value of h smaller than ours, and found many more cases of large second differences. In quantum mechanical perturbation theory calculation,[20a] we also observed many more "zeroth order crossings" (which yield avoided crossings upon use of degenerate perturbation theory near the crossing) for Pomphrey's h than for ours. Similarly, in classical perturbation theory calculations for the Barbanis potential, we have found, using a grid of action variables, an onset of "zeroth order crossings" roughly at an energy where classical "chaos" begins.[20b]

Stratt, Handy and Miller[21] in their investigation of the Barbanis potential studied nodal patterns of quantum mechanical wavefunctions and found for some states major changes of nodal patterns. We believe, and are currently testing this possibility, that these changes are each associated with avoided crossings. In this study, it will be interesting to see whether the latter are isolated avoided crossings or overlapping ones. (Only the latter may prove to be associated with "chaotic" behavior.[19])

Nordholm and Rice[22] studied the wavefunctions ψ for the Hénon-Heiles potential and examined their projections on those of the unperturbed (harmonic oscillator) basis set. When a ψ was substantiall distributed over a number of the latter states, it was termed "global and was termed local otherwise. So defined, a state can appear to be global not only when its wavefunction is "statistical" (sometimes labeled 'stochastic', 'ergodic', 'chaotic'), but also when its shape is considerably distorted from the corresponding one of the unperturbed system. Indeed we were actually able to find classically the invariant tori, each of which corresponded individually semiclassically to many of the quantum states that had been termed "global", so that all of these particular global states certainly are of the second case, i.e. nonchaotic. Even though globality is, therefore, not necessarily, or even primarily, due to chaotic behavior, it is very interesting in its own right. It provides information on the nature of the wavefunction relative to that of some unperturbed system. Because of the basis set dependence of global vs. local states, similar calculations were made using natural orbitals as the basis set.[20] The comparison is still, to be sure, a coordinate dependent one.

IV. APPLICATIONS OF QUASIPERIODIC AND CHAOTIC BEHAVIOR

Scattering Processes

Scattering resonances receive much attention in the quantum dynamics literature and can contribute significantly to the total cross section of a scattering process. They are also an important source of disagreement between quasiclassical and fully quantum mechanical scattering calculations. A standard method of locating these resonances has been quantum mechanical scattering calculations.[23] However, when the resonances are very narrow (as in the following system reviewed in this paper), a quantum calculation faces a time-consuming and difficult task in locating each one. Alternatively, as the dimensionality of the problem increases, the quantum mechanical solution becomes correspondingly more difficult. Motivated by this difficulty, the variational approach (stabilization method)[24] was used by Eastes and Marcus[25] to locate resonances. They compared this variational calculation to an exact quantum mechanical calculation.

The compound state resonance studied arose from the coupling of a Morse interaction potential, which monotonically goes to the dissociation limit from the bottom of the well, to a harmonic oscillator A new semiclassical location of resonance energies[26] was recently made, which utilizes the Poincaré surface of section quantization of

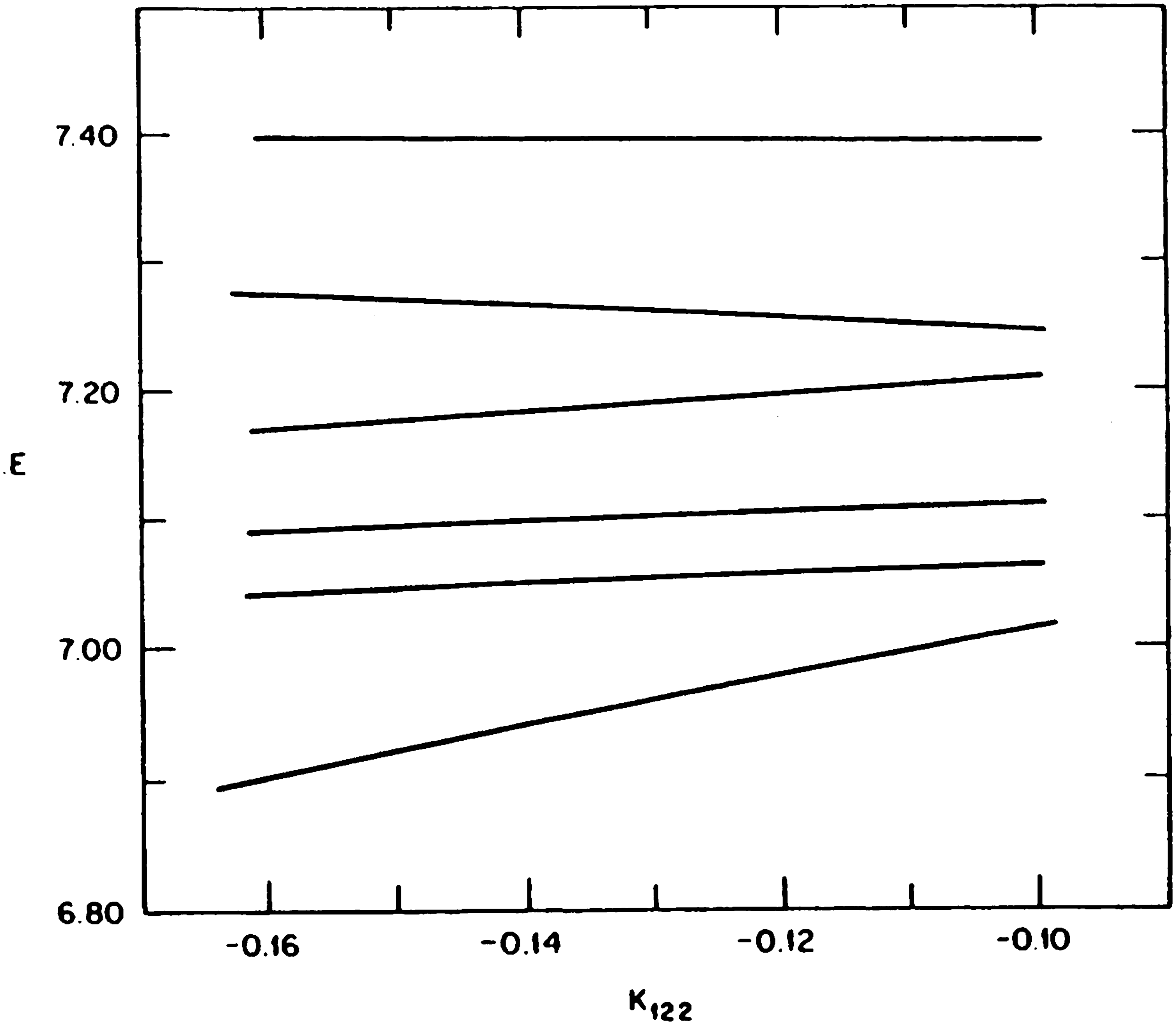

Fig. 16. A correlation diagram of the eigenvalue spectra for Hamiltonian (III-2) for the quasiperiodic regime.

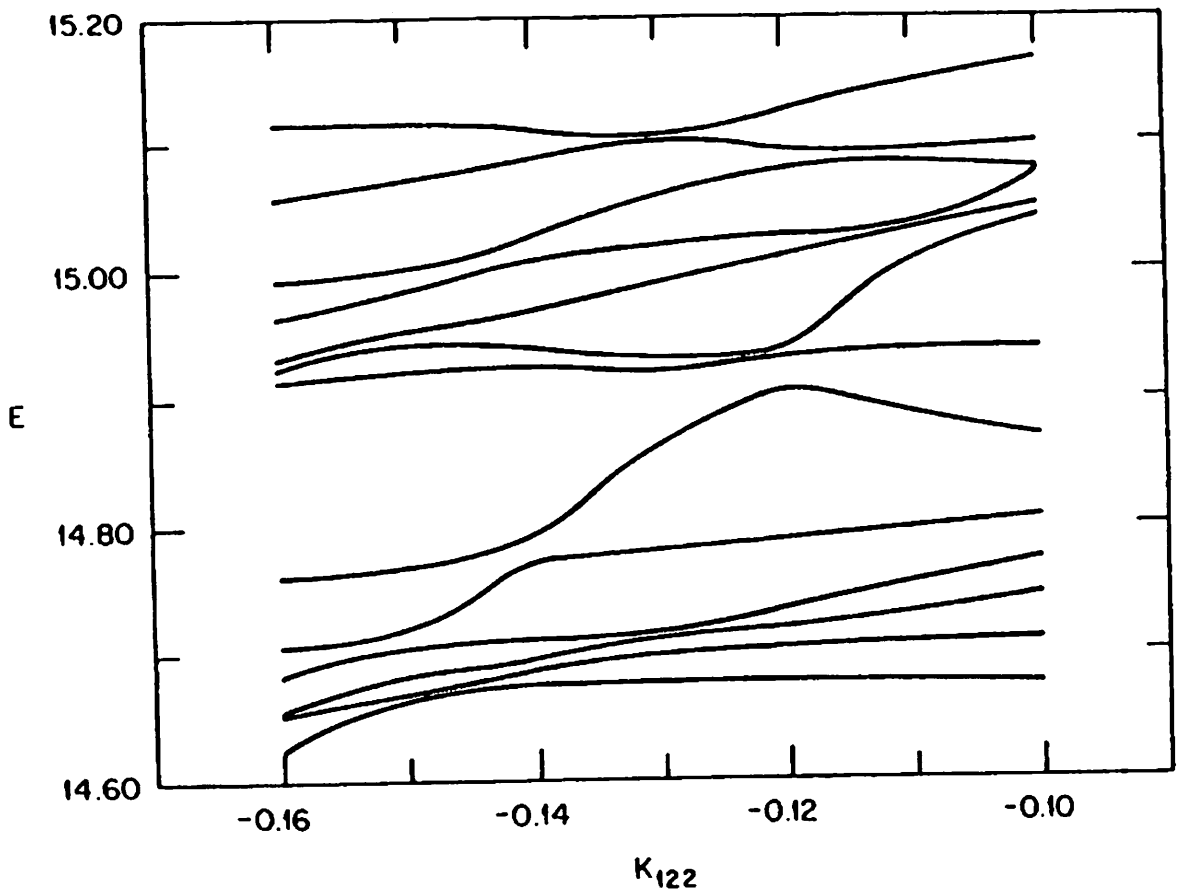

Fig. 17. As in Fig. 16, but for the chaotic regime.

the classical action integral. The eigentrajectories (trajectories with the correctly quantized actions) then correspond to quantum quasibound states; therefore, their energies correspond to the resonance energies.

The model Hamiltonian used was

$$H = \frac{p_x^{2}}{m} + p_y^{2} + y^{2} + De^{-\alpha(x-y)} - 2De^{-\alpha(x-y)/2} \qquad \text{(IV-1)}$$

which corresponds to a collision between a harmonic oscillator and a particle with a Morse interaction potential, where D is the depth, m is a mass ratio, and α is the steepness of the potential between the colliding partners. The parameters are the same as those in Ref. 25.

The Hamiltonian (1) will support no bound states along the exit channel (essentially the x coordinate) for energies greater than D, the dissociation limit of the Morse oscillator. However, even at such energies, some classically bound states of the entire system can be located, because of their quasiperiodic motion. An example is the trajectory in Fig. 18. They were then quantized using the Poincaré surface of section semiclassical method described earlier. Excellent agreement for the positions of the resonances was found between the semiclassical and full quantum results. Where no scattering resonances were found in Ref. 25, the trajectories did not produce quasiperiodic surfaces of section, but instead drifted, leading to escape of the particle. Such a chaotic type of unbound trajectory is shown in Fig. 19.

The existence of these two radically different types of motion (quasiperiodic and chaotic) led us to believe that there would be a change in the behavior of the inelastic cross section when the internal vibrational motion of one of the scattering partners reached the stochastic regime. One example with no observed effect has been reported.[27] We have also investigated this problem with a model consisting of a vibrator with two degrees of freedom undergoing a collinear collision with an atom.[28] The Hamiltonian for a system which exhibits more delocalized motion in the chaotic regime than that of Ref. 27 is

$$H = H_{vib} + H_p \qquad \text{(IV-2a)}$$

where

$$H_{vib} = \frac{p_x^{2}}{m} + p_y^{2} + y^{2} + D\left(\exp - 2\gamma(x-y) -2 \exp -\gamma(x-y)\right) \qquad \text{(IV-2b)}$$

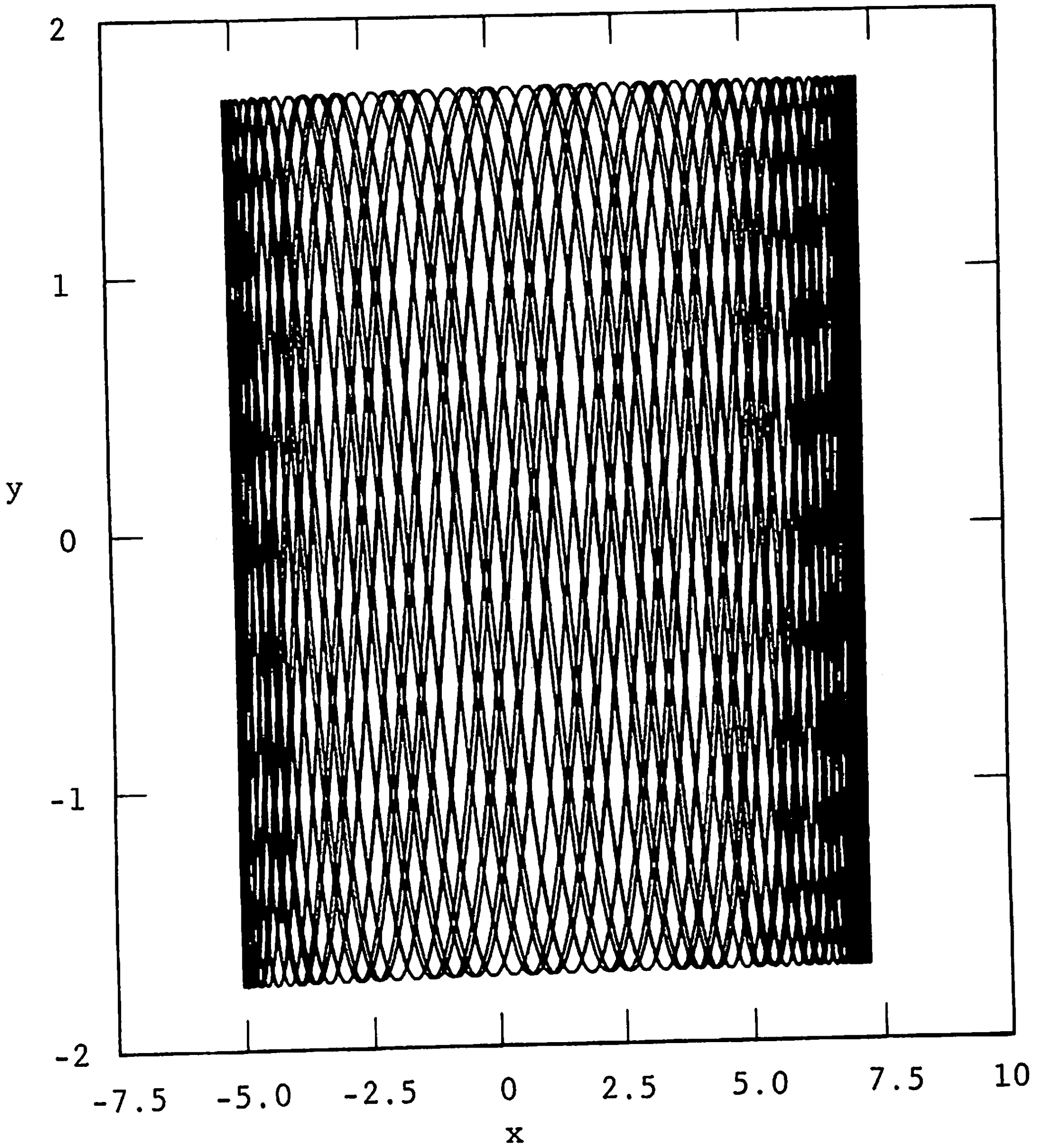

Fig. 18. A quasibound quasiperiodic trajectory for Hamiltonian (IV-1).

and

$$H_p = p_z^{\,2} + 4\varepsilon\left(\left(\sigma/(z-x)\right)^{12} - \left(\sigma/(z-x)\right)^{6}\right) \qquad \text{(IV-2c)}$$

with D = 10.0, $\gamma = 0.25$, $\varepsilon = 1.0$, and $\sigma = 1.0$. For large z, this Hamiltonian reduces to that of a free particle and a harmonic oscillator coupled to a Morse oscillator.

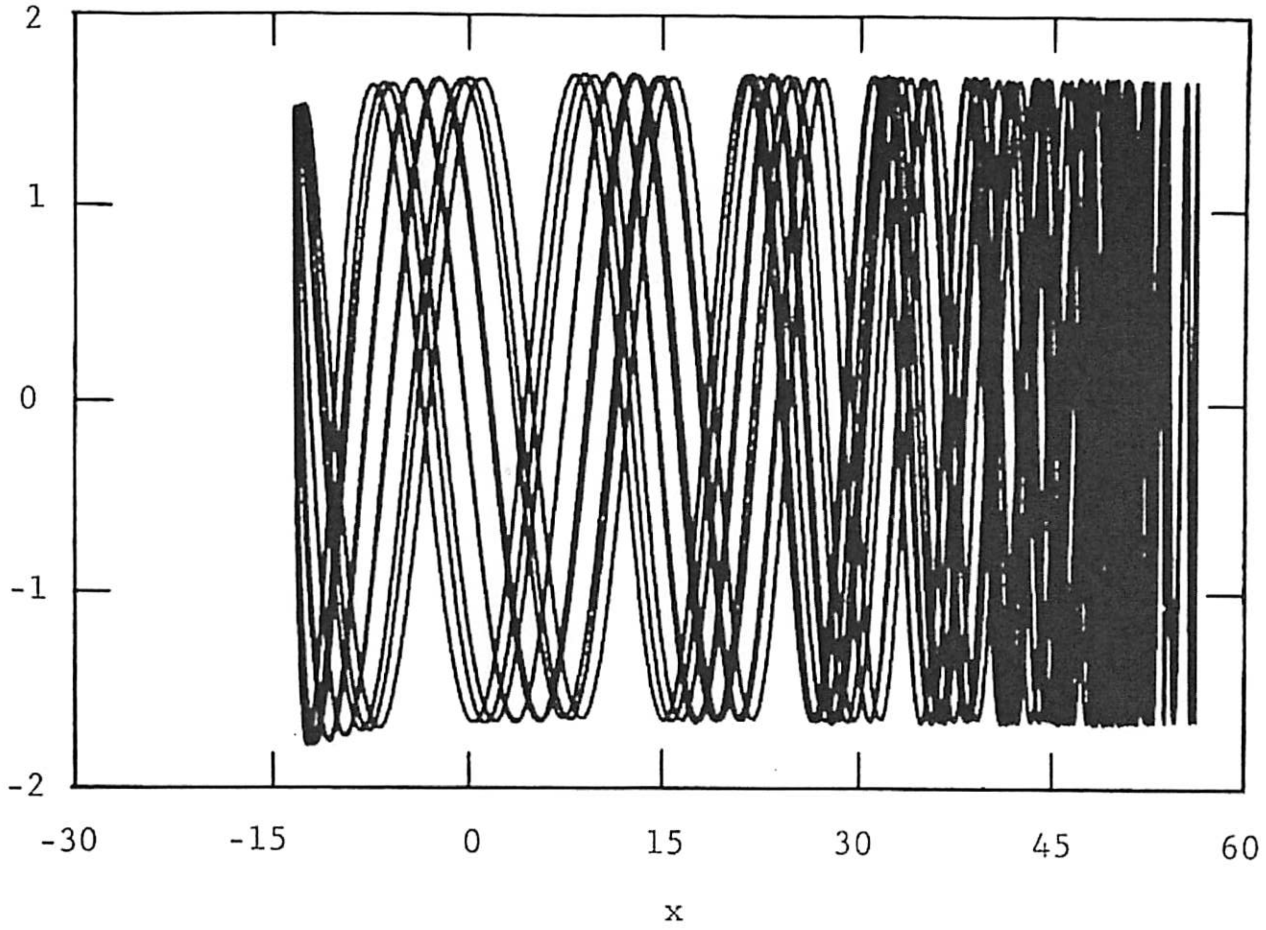

Fig. 19. A trajectory for Hamiltonian (IV-1) which is slowly leaking out to large x.

A trajectory for the molecular part of Hamiltonian (IV-2b), when the atom and molecule are far apart, is shown in Fig. 20 for the quasiperiodic regime and in the chaotic regime in Fig. 21. In order to investigate the scattering process, we calculated the average of the square of the energy transfer. The translational and "x-mode" vibrational energies were kept constant, and the average was calculated with 1000 trajectories over the vibrational phases. Fig. 22 shows the results as a function of total vibrational energy of the molecule E_M at two different translational energies. Fig. 22 shows that when the vibrational motion changes to chaotic (above $E \geqslant -2.5$), there is a difference in the behavior of the energy transfer probability. More detailed studies of this phenomenon are currently underway.

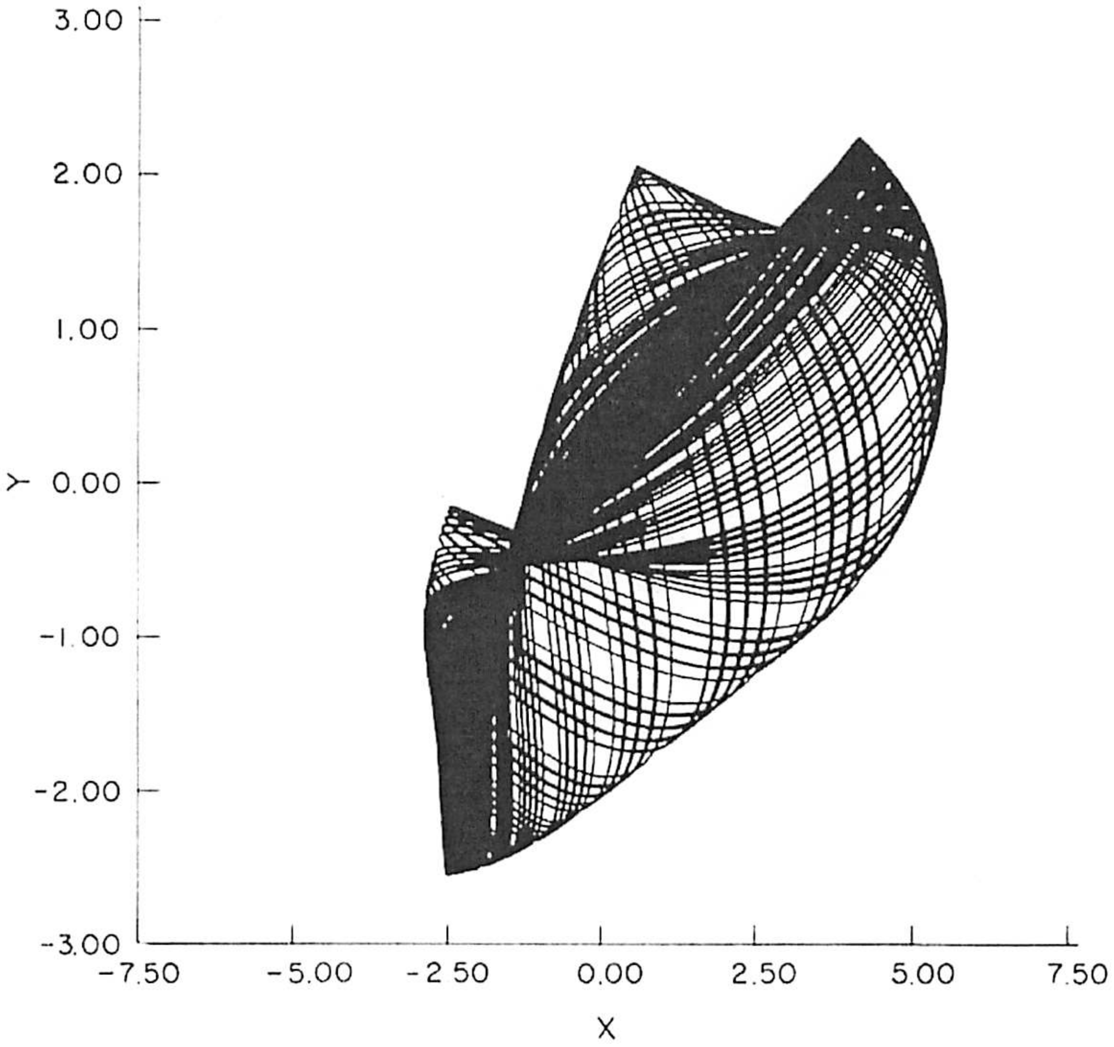

Fig. 20. Quasiperiodic trajectory for Hamiltonian (IV-2b) with $E = -3.5$.

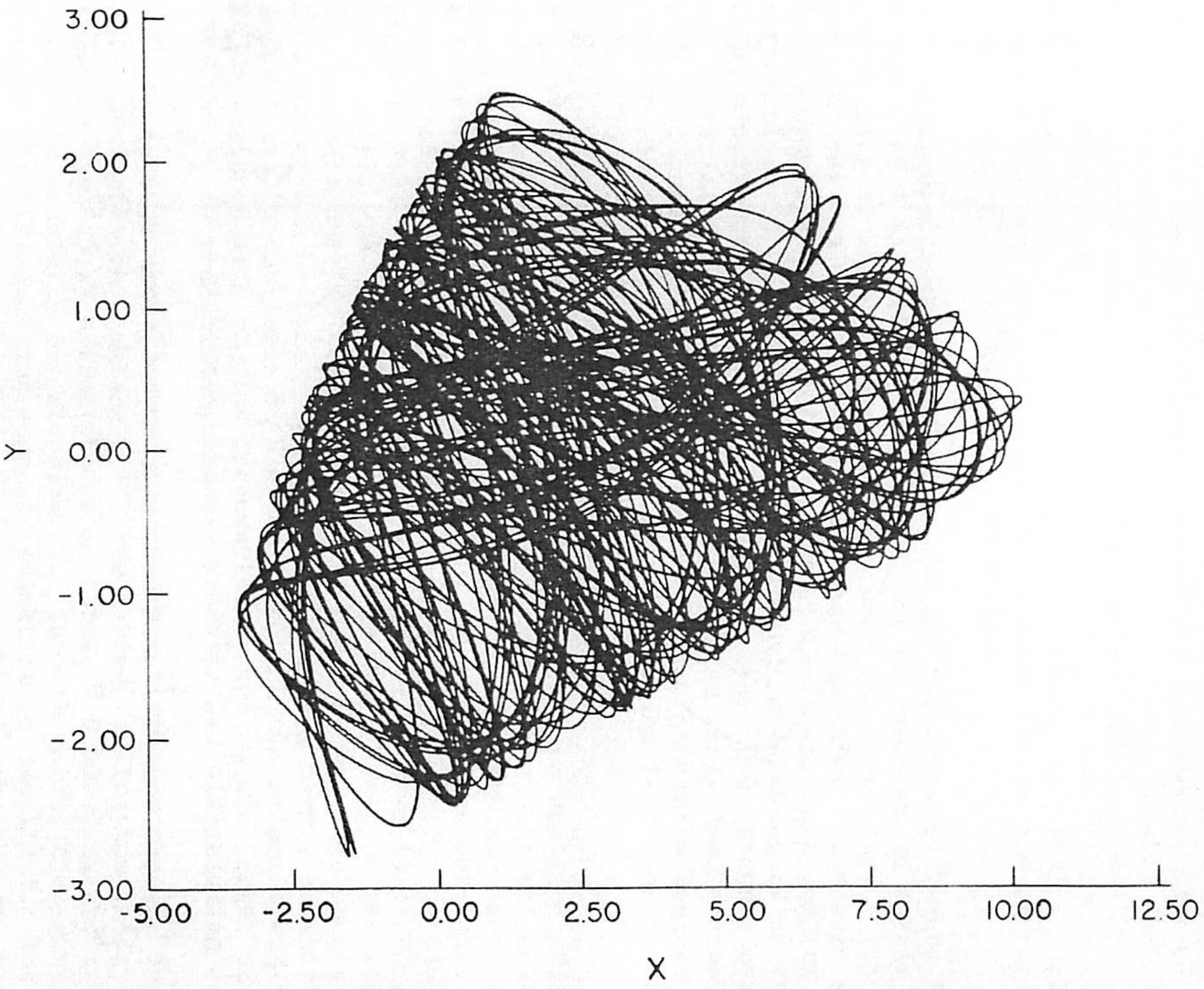

Fig. 21. Chaotic trajectory for Hamiltonian (IV-2b) with E = -1.5.

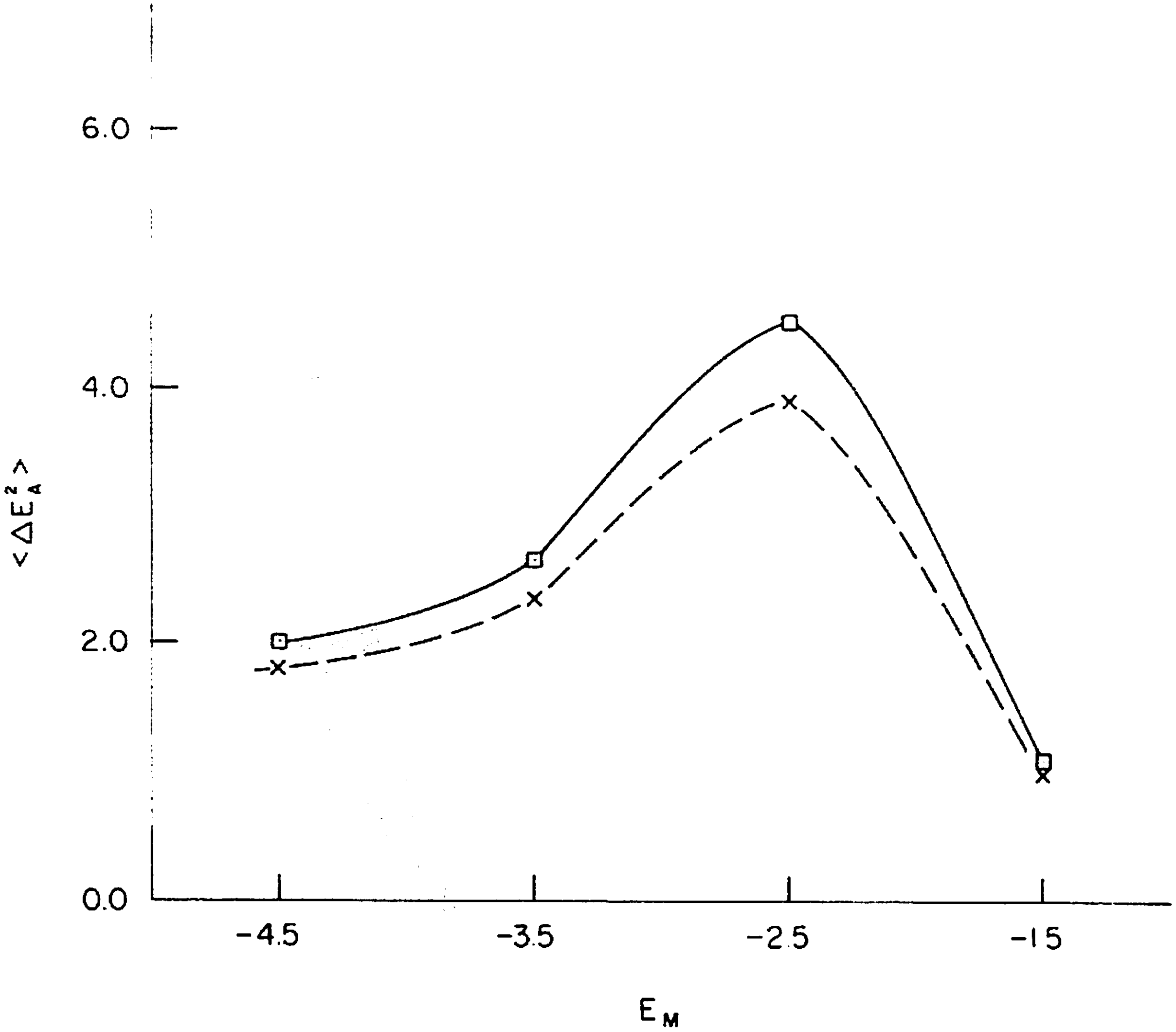

Fig. 22. Plot of $<\Delta E^2>$ for the collinear collision of a particle and triatomic molecule.

Infrared Multiphoton Dissociation

There has been considerable interest in infrared multiphoton dissociation processes during the past few years.[29-37] Particularly interesting experimental results have recently been obtained in which two infrared lasers of different powers and frequencies have been used to dissociate polyatomic molecules.[30] Their results indicate that polyatomic molecules may be dissociated much more easily (lower powers) by the use of two lasers than with just one.[30] These experiments also demonstrate that isotopic selectivity is significantly enhanced and that two-laser multiphoton dissociation may be more ideally suited for laser isotope separation.

We investigated the effect of one and two infrared lasers interacting with a diatomic molecule,[33,34] and we examined in detail the probability of dissociation for cases when the laser powers are equal and when one has a much higher power than the other. Although a model Hamiltonian was used to represent the diatomic molecule and its interaction with the lasers, the conclusions are analogous to those found experimentally for polyatomic molecules: the diatomic molecule was dissociated much more easily by using two laser frequencies than with just one. Recent results from nonlinear mechanics suggest that this two-laser effect may be due to a transition from quasiperiodic motion to a chaotic type motion.

Similar calculations were performed on a more realistic Hamiltonian where the parameters used correspond to the diatomic molecule being hydrogen fluoride.[34] It was found that in the two-laser case, a different type of dynamics occurs as opposed to the one-laser. An example of the one-laser energy adsorption as a function of time is shown in Fig. 23. The corresponding plot for the two-laser case is shown in Fig. 24. An explanation of this process may be the result of resonance overlap caused by the two-laser terms. The process has been postulated by Ford[15] and Chirikov[38] to be a source of stochastic instability in nonlinear mechanics. When the two resonant widths, $\Delta\omega$, associated with the two frequencies ω_1 and ω_2 are large, and when the ω_2 is red-shifted, chaotic behavior and dissociation occur.

In another study, we modeled the IR multiphoton process for a model of a triatomic molecule.[39] The maximum excitation energy is shown in Fig. 25 as a function of ω_I for E_I = 0.05, 0.10 and calculated both quantally and classically. In both cases, the agreement between the classical and quantal excitation is excellent. The only differences between the two calculations are (i) the quantal excitation falls more abruptly on the red side of the peak; (ii) the quantal threshold for dissociation is slightly higher than the classical. These effects may reflect the greater difficulty of exciting the discrete quantum levels, especially in the earlier states of excitation.

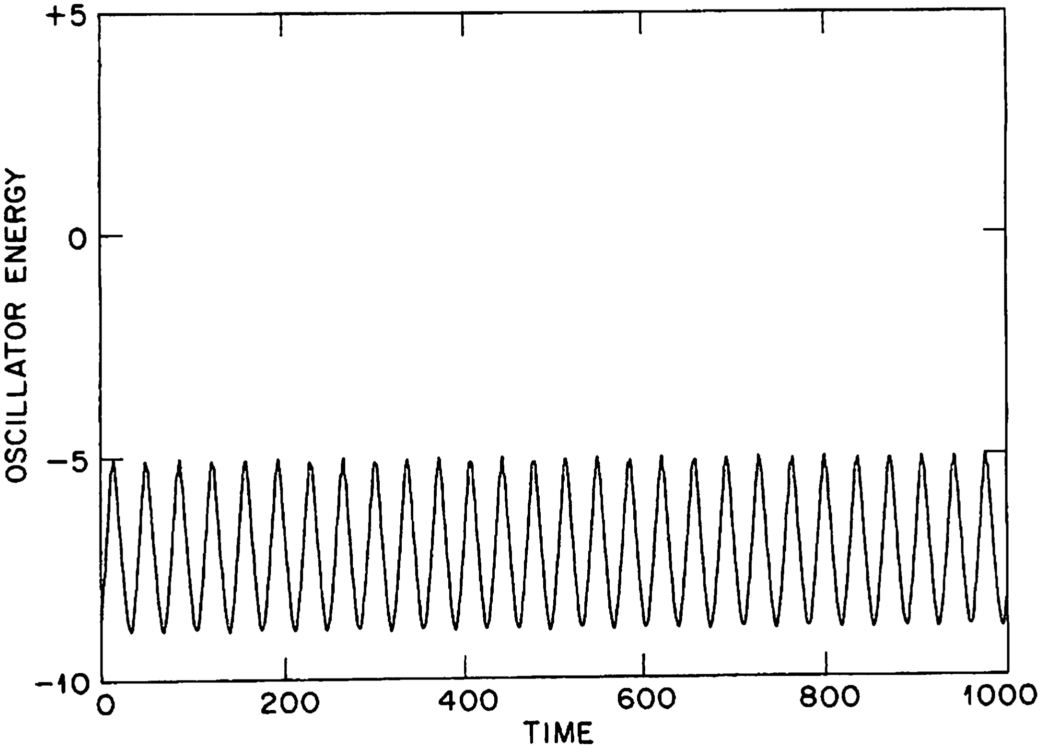

Fig. 23. Energy as a function of time for one-laser excitation.

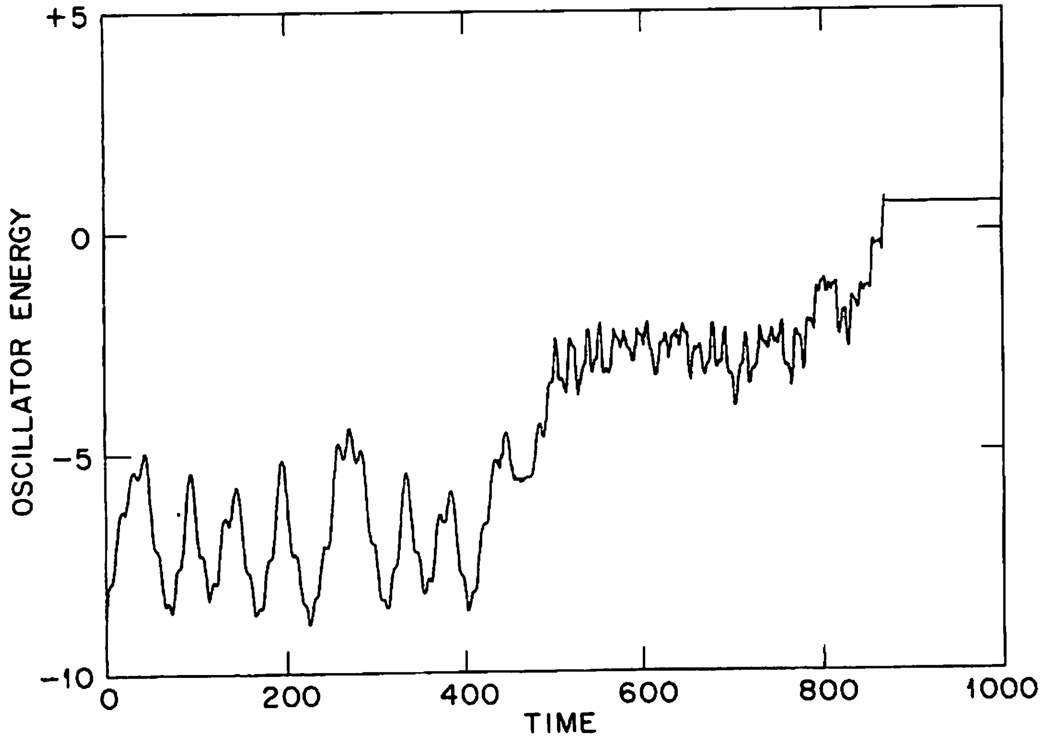

Fig. 24. Energy as a function of time for two-laser excitation.

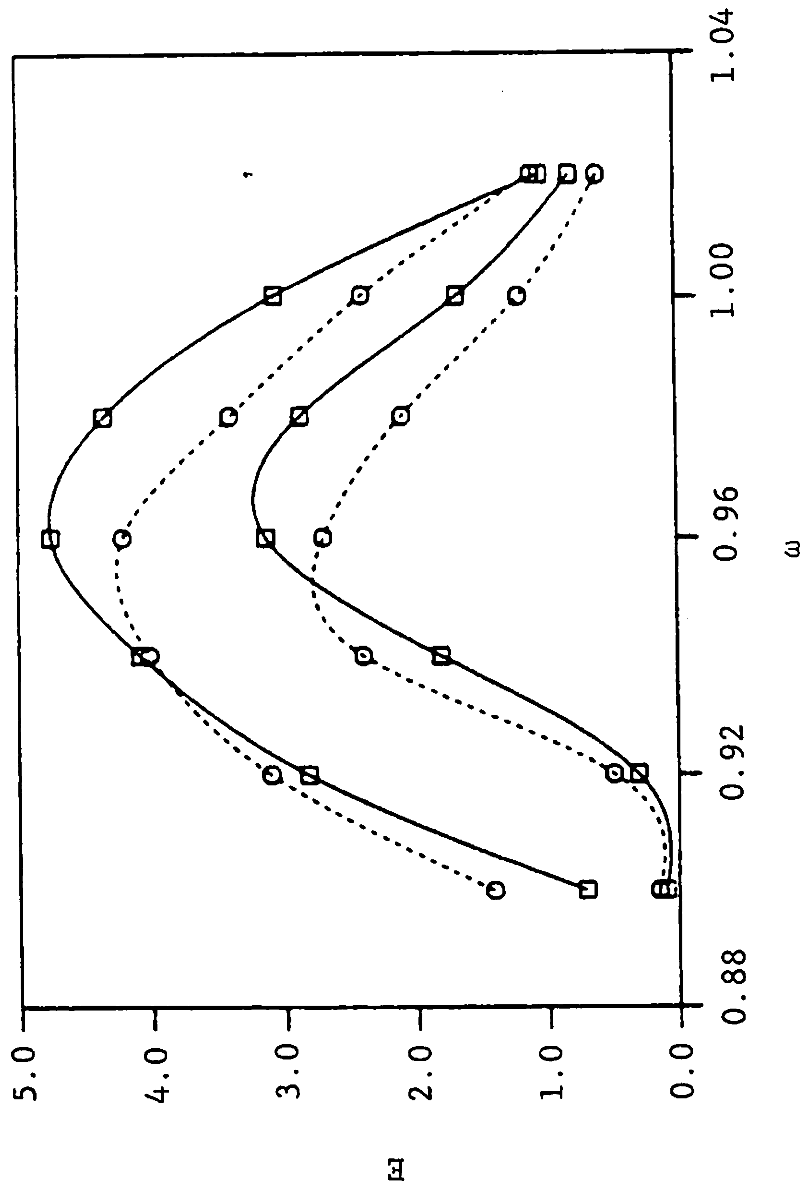

Fig. 25. A comparison of classical (circles) and quantum (squares) maximum excitation at two laser powers.

Franck-Condon Factors

The Franck-Condon factor[40] for transitions between different electronic states has recently been expressed in terms of the Wigner distribution function.[41] The various cases for quasiperiodic and stochastic type classical motion were considered.[42] It was found that the Wigner function is represented by very different types of functions in the quasiperiodic regimes.[43,44]

It was shown that in the classical limit, evaluation of the Franck-Condon factor requires solution of the dynamics if the vibrational state is quasiperiodic; in the chaotic regime, the Franck-Condon factor depends only on the global structure of the interaction surface.

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References

1. E.g. (a) J. B. Keller, Ann. Phys. (NY) 4:180 (1958).
   (b) M. V. Berry, Ann. Phys. (in press).
2. For a review of other methods, see I. C. Percival, Adv. Chem. Phys. 36:1 (1977).
3. M. Tabor, Adv. Chem. Phys. (in press).
4. (a) R. A. Marcus, Discuss. Faraday Soc. 55:34 (1973).
   (b) W. Eastes and R. A. Marcus, J. Chem. Phys. 61:4301 (1974).
   (c) D. W. Noid and R. A. Marcus, J. Chem. Phys. 62:2119 (1975).
   (d) D. W. Noid and R. A. Marcus, J. Chem. Phys. 67:559 (1977).
   (e) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, J. Chem. Phys. 71:2864 (1979).
   (f) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, J. Chem. Phys. 73:0000 (1980).
   (g) R. A. Marcus, D. W. Noid, and M. L. Koszykowski, "Semiclassical Studies of Bound States and Molecular Dynamics," in: Stochastic Behavior in Classical and Quantum Hamiltonian Systems, Volta Memorial Conference, Como, Italy, 1977, G. Casati and J. Ford, eds., Lecture Notes in Physics, Vol. 93, Springer Verlag, New York (1978/79) 283.
5. M. Toda, Phys. Lett. A 48:335 (1974).
   P. Brumer and J. W. Duff, J. Chem. Phys. 65:3566 (1976); ibid. 67:4898.
6. D. W. Noid, M. L. Koszykowski, M. Tabor, and R. A. Marcus, J. Chem. Phys. 72:6169 (1980).
7. D. W. Noid, M. L. Koszykowski, and R. A. Marcus, J. Chem. Phys. 67:404 (1977).

8. M. L. Koszykowski, D. W. Noid, and R. A. Marcus, *J. Chem. Phys.* (to be submitted).
9. K. Hansel, *Chem. Phys.* 33:35 (1978).
10. G. E. Powell and I. C. Percival, *J. Phys. A* 12:2053 (1979).
11. E. J. Heller, *Chem. Phys. Lett.* 60:338 (1979).
12. M. L. Koszykowski, D. W. Noid, M. Tabor, and R. A. Marcus, *J. Chem. Phys.* 73:0000 (1980).
13. K. C. Mo, *Physica* 57:455 (1972).
14. M. L. Koszykowski, D. W. Noid, and R. A. Marcus (to be submitted).
15. E.G., J. Ford, *Adv. Chem. Phys.* 24:155 (1973), and references cited therein.
16. I. C. Percival, *J. Phys. B* 6:559 (1973).
17. N. Pomphrey, *J. Phys. B* 7:1909 (1974).
18. D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Chem. Phys. Lett.* (in press).
19. R. A. Marcus, "Horizons in Quantum Chemistry," Proc., Third International Conference on Quantum Chemistry, Kyoto, Japan, Oct. 29-Nov. 3, 1979, eds. K. Fukui and B. Pullman, Reidel, Dordrecht, Holland (1980); R. A. Marcus, *Ann. N. Y. Acad. Sci.* (in press).
20. (a) R. Ramaswamy and R. A. Marcus, *J. Chem. Phys.* (submitted).
    (b) R. Ramaswamy and R. A. Marcus, *ibid.* (submitted).
21. R. M. Stratt, N. C. Handy, and W. H. Miller, *J. Chem. Phys.* 71:3311 (1979).
22. S. Nordholm and S. A. Rice, *J. Chem. Phys.* 61:768 (1974); *ibid.* 62:157 (1975).
23. D. Secrest, *Ann. Rev. Phys. Chem.* (1973).
24. J. R. Taylor, *Scattering Theory*, John Wiley, New York (1972).
25. W. Eastes and R. A. Marcus, *J. Chem. Phys.* 59:4757 (1973).
26. D. W. Noid and M. L. Koszykowski, *Chem. Phys. Lett.* 73:114 (1980).
27. G. Schatz and T. Mulloney, *J. Chem. Phys.* 71:5257 (1979).
28. D. W. Noid and M. L. Koszykowski, *Chem. Phys. Lett.* (in press).
29. R. V. Ambartzumian and V. S. Letokhov, in: *Chemical and Biochemical Applications of Lasers*, Vol. III, ed. C. B. Moore, Academic Press, New York (1977).
30. D. K. Evans, R. D. McAlpine, and F. K. McClusky, *Chem. Phys. Lett.* 65:226 (1979).
31. D. W. Noid, M. L. Koszykowski, R. A. Marcus, and J. D. McDonald, *Phys. Lett.* 51:540 (1977).
32. R. A. Marcus, D. W. Noid, and M. L. Koszykowski, in: *Advances in Laser Chemistry*, ed. A. H. Zewail, Springer, New York (1978) 298.
33. D. W. Noid and J. R. Stine, *Chem. Phys. Lett.* 65:153 (1979).
34. J. R. Stine and D. W. Noid, *Optics Comm.* 31:161 (1979).
35. R. Walker and R. Preston, *J. Chem. Phys.* 67:2017 (1977).
36. K. D. Hansel, *Chem. Phys. Lett.* 57:619 (1978).
37. D. Poppe, *Chem. Phys.* 45:371 (1980).
38. B. V. Chirikov, *Reports of Physics* 52:263 (1979).

39. D. W. Noid, C. Bottcher, and M. L. Koszykowski, Chem. Phys. Lett. 72:397 (1980).
40. R. W. Nicholls and A. L. Stewart, in: Atomic and Molecular Processes, ed. D. R. Bates, Academic Press, New York (1962).
41. E. P. Wigner, Phys. Rev. 40:749 (1932).
42. W.-K. Liu and D. W. Noid, Chem. Phys. Lett. (in press).
43. M. V. Berry, Phil. Trans. Royal Soc. A 287:237 (1977).
44. M. V. Berry, J. Phys. A 10:2083 (1977).