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

Methods for Plotting Trajectories for Triatomic Molecules and Visualizing the Caustics

D. W. Noid,† D. M. Wardlaw,‡ M. L. Koszykowski,⊥ and R. A. Marcus*

Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, Arthur Amos Noyes Laboratory of Chemical Physics, California Institute of Technology, Pasadena, California 91125, and Sandia National Laboratory, Livermore, California 94550 *(Received: January 3, 1983)*

A simple and efficient computational method is introduced for visualizing the structure of three-dimensional classical trajectories. Examples are presented for Hamiltonians with incommensurate frequencies, as well as with 1:1 and 2:1 resonances. Results are also presented for several states of OCS, one of which shows an accidental 4:1 resonance. Implications of this method for path integral quantization and perturbation methods are discussed.

Preface

Henry Eyring was one of the pioneers in the recent theory of chemical reaction rates. R.A.M. was fortunate to know him for some three decades, and to see the joyousness with which he approached his science and his interactions with people. In recent years there has been an increasing amount of interest in the field of intramolecular dynamics and the anharmonic motion of vibrations, subjects related to one of Henry's interests—the statistical theory of mass spectral decomposition patterns. It is a pleasure to dedicate this article to his memory.

Introduction

Nonlinear dynamics has been the subject of intense study in recent years, and semiclassical methods have been developed to treat bound and quasibound states of multidimensional nonseparable systems.[1,2] Most studies have focused on coupled two-oscillator systems. The two principal methods used for describing the trajectories in two-oscillator systems have been (1) plots of the trajectories themselves in various coordinates and (2) plots of Poincaré surfaces of section in various coordinates. It appeared at first that both of these techniques would be difficult to extend to three-oscillator systems. The surface of section technique has been extended to three-coordinate systems for maps[3] and for trajectories,[4] and can similarly be extended to four coordinates. In the present paper we extend the trajectory plots to three dimensions in a way which permits visualization of shapes for use in semiclassical quantization and for identification of resonances.

Examples of three-oscillator systems include nonrotating linear and nonrotating nonlinear triatomic molecules, as well as a time-independent form of a two-laser driven oscillator.[5] Although the 3-D Poincaré surface of section technique[4] is useful in studying the dynamics, there is a prerequisite for performing the semiclassical quantization: suitable paths for evaluation of the phase integrals depend on the shape of the trajectories, namely, on the caustics, which are, in turn, affected by internal resonances. It is highly desirable, therefore, to have a meaningful picture of the several-dimensional trajectory itself, in particular one which depicts the caustics. In this exploratory paper a method is devised for this purpose. It is described in section II, and several applications are given in section III. The method is expected to be useful for quantization methods which use the trajectories themselves. It should also be useful for perturbation methods in which one tacitly assumes the nature of the caustics, which them-

† Oak Ridge National Laboratory.
‡ Authur Amos Noyes Laboratory of Chemical Physics. NSERC of Canada Postdoctoral Research Fellow.
⊥ Sandia National Laboratory.
* Author to whom correspondence should be addressed at the Author Amos Noyes Laboratory of Chemical Physics. Contribution No. 6769.

(1) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Annu. Rev. Phys. Chem.*, 32, 267 (1981).
(2) M. Tabor, *Adv. Chem. Phys.*, 46, 73 (1981); P. Brumer, *ibid.*, 47, 201 (1981); S. A. Rice, *ibid.*, 47, 117 (1981).
(3) C. Froeschle, *Astrophys. Space Sci.*, 14, 110 (1971).
(4) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.*, 73, 391 (1980).
(5) J. R. Stine and D. W. Noid, *J. Phys. Chem.*, 86, 3733 (1982).

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selves depend on the presence and spatial structure of resonant trajectories.

Methods

By solving Hamilton's equations

$$\dot{Q}_i = \partial H/\partial P_i \qquad \dot{P}_i = -\partial H/\partial Q_i \tag{1}$$

with subroutine DEROOT,[6] one can calculate, as described below, the values of (Q_1, Q_2) for which Q_3 is some constant value. In this way, one can find data for a plane (Q_3 = constant) of a 3-D trajectory in (Q_1, Q_2, Q_3) space. Because the display of these (Q_1, Q_2) as points would require a large number of such points to visualize the structure of a trajectory, the values of (Q_1, Q_2) are binned in a two-dimensional array. When a quasiperiodic trajectory is propagated to increasingly longer times, the number of filled bins in this (Q_1, Q_2) space begins to stabilize, i.e., the trajectory enters no new bins. The technique is readily implemented: DEROOT automatically determines values for which some function G (defined by the user) is zero. For the $Q_3 = 0$ plots, we set $G = Q_3$. For our purposes, we consider 100 bins of Q_1 and 100 bins of Q_2. In the plots we use one symbol (+) to denote a filled bin in (Q_1, Q_2) space, and either use another symbol (0) [Figures 1–3], or a contour where the potential energy equals the total energy [Figures 5–8], to indicate the classically forbidden region. In this way, a cross section of the 3-D trajectory can be plotted. This information on which bin is filled for any Q_3 is stored in an integer array with $(10^2)^2$ numbers. (Even a minicomputer can be used. If storage is a problem the information can be packed into words.)

It is also useful to make a second type of plot, using the approach of Ashton and Muckerman,[7] by constructing (Q_1, Q_2) cross sections at different values of Q_3. In this case, we set

$$G = \prod_{i=1}^{100}(Q_3 - C_i) \tag{2}$$

and solve for the zeroes of this G using the DEROOT program. As before, the information is stored in an integer array, but now with $(10^2)^3$ values when 100 Q_3's are considered.

The collection of bins can be plotted in a 3-D perspective by using the plotting package DISPLA[8] (we use below a symbol 0 to denote a filled bin). To visualize the trajectory we have found it useful to change the viewpoint by rotating past the object in the Q_1Q_2 plane at a fixed distance and height above it. These several views from different angles will be termed a "fly-by".

Model Hamiltonians and Results

Several model Hamiltonians are used below for illustration, the first being

$$H = \tfrac{1}{2}(P_1^2 + P_2^2 + P_3^2 + \omega_1^2Q_1^2 + \omega_2^2Q_2^2 + \omega_3^2Q_3^2) + \lambda(Q_1Q_2^2 - \eta Q_1^3) + \lambda(Q_2Q_3^2 - \eta Q_2^3) \tag{3}$$

Trajectories for the case in which ω_1, ω_2, and ω_3 are incommensurate are considered first, with $\omega_1 = 0.7$, $\omega_2 = 1.3$, $\omega_3 = 1.0$, $\lambda = -0.1$, and $\eta = 0.1$. The slice $Q_3 = 0$ is plotted in Figure 1 for the zeroth order state (1,0,1) in ref 4. The trajectory is seen to be "boxlike", as expected.

For the case $\omega_1 = 1.4$, $\omega_2 = 0.7$, and $\omega_3 = 1.0$ the trajectory exhibits a 2:1 Fermi resonance in the $Q_3 = 0$ plane.

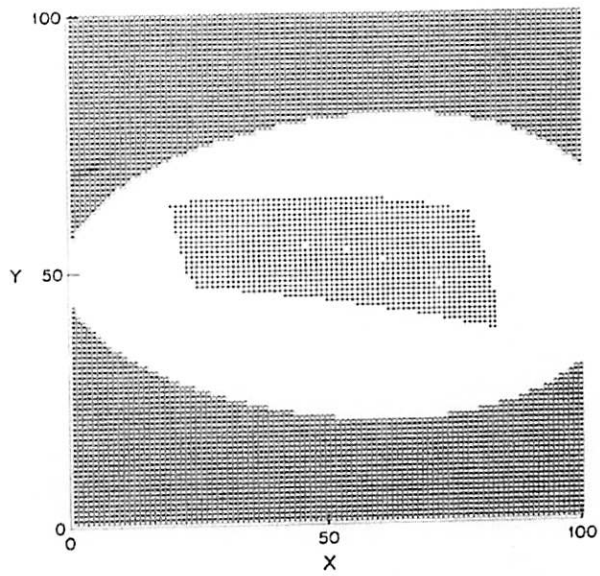

Figure 1. View of the Q_1, Q_2 plane at $Q_3 = 0$ for an incommensurate Hamiltonian. The labels X, Y, and Z correspond to Q_1, Q_2, and Q_3, respectively. In Figures 1–3 the initial conditions were determined from the unperturbed Hamiltonian as follows: total energy $E = E_1 + E_2 + E_3$, with $E_i = (n_i + {}^1/_2)\,\omega_i$, $Q_i = 0$, and $P_i = (2E_i)^{1/2}$, $i = 1, 2, 3$. Here $E = 3.2$ and $(n_1,n_2,n_3) = (1,0,1)$.

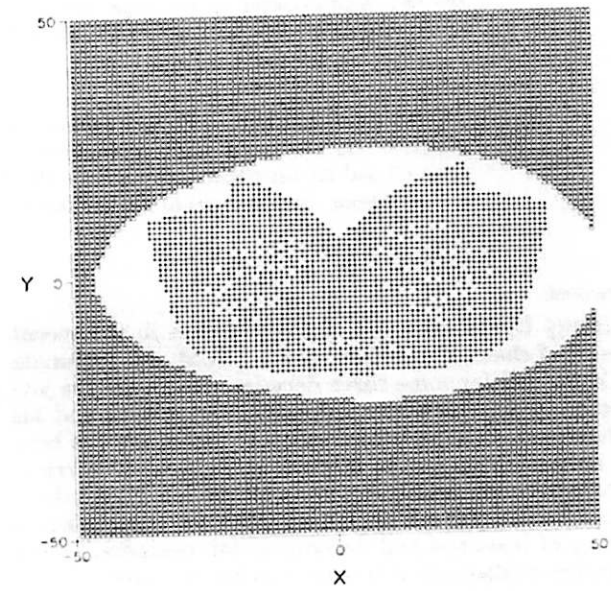

Figure 2. Same as Figure 1, but with a Fermi resonance interaction; $E = 2.5$, initial actions were not chosen to correspond to integers.

This slice is shown in Figure 2 for arbitrary zeroth order actions and is of a shape similar to those found for 2-D 2:1 resonant systems[9] (formed from librating figure eights). Thus, the technique shows that the quantization method used in those systems could be applied to the present system.

In Figure 3 is shown a $Q_3 = 0$ slice for the case $\omega_1 = \omega_2 = \omega_3 = 1$. The trajectory, which has arbitrary zeroth order actions, is of the librating type and is similar to those found in the 1:1 2-D system.[10] This trajectory also resembles the local mode type found by Lawton and Child[11] in a

(6) L. F. Shampine and M. K. Gordon, "Computer Solution of Ordinary Differential Equations: The Initial Value Problem", W. A. Freeman, San Francisco, 1975.
(7) C. J. Ashton and J. T. Muckerman, *J. Phys. Chem.*, this issue.
(8) The DISPLA plotting package is prepared by Integrated Software Systems Corporation, San Diego, CA 92121.
(9) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.*, 71, 2864 (1979).
(10) D. W. Noid and R. A. Marcus, *J. Chem. Phys.*, 67, 559 (1977).
(11) R. Lawton and M. S. Child, *Mol. Phys.*, 37, 1799 (1979); R. M. Hedges and W. P. Reinhardt, *Chem. Phys. Lett.*, 91, 241 (1982).

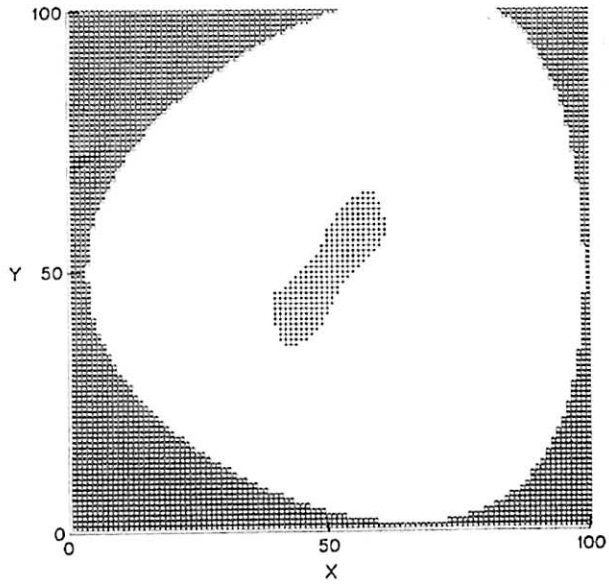

Figure 3. Same as Figure 1, but for a librating trajectory of a 3-D Henon–Heiles Hamiltonian; $E = 5.0$, initial actions were not chosen to correspond to integers.

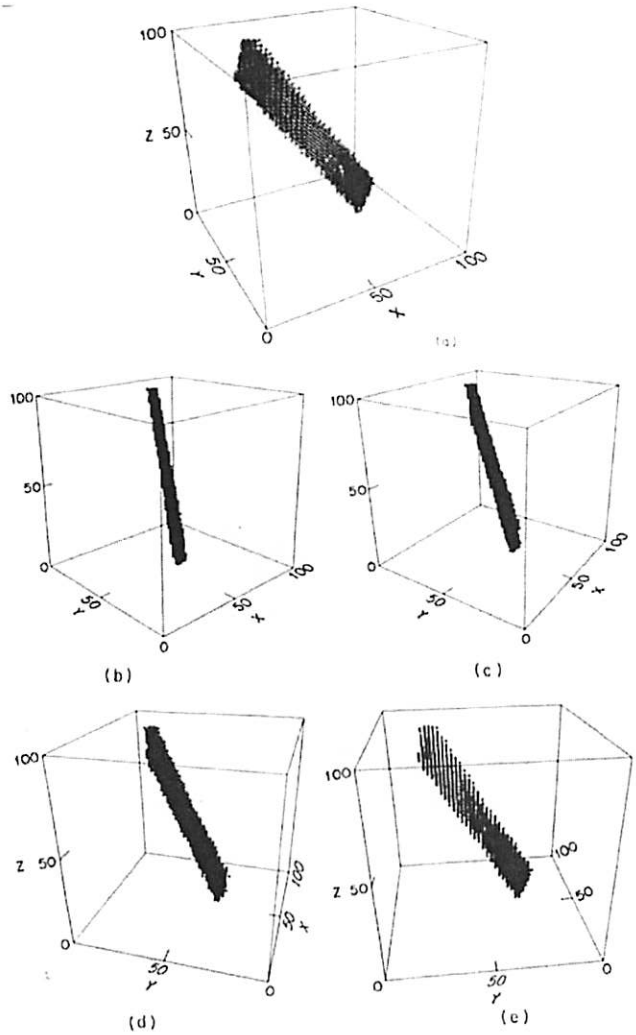

Figure 4. Fly-by views of the trajectory in Figure 3. The successive views correspond to counter-clockwise rotation of the cube about its Z axis.

two-coordinate system. A 3-D "fly-by" of this trajectory is given in Figure 4, and the spatial orientation of the 3-D trajectory can clearly be seen.

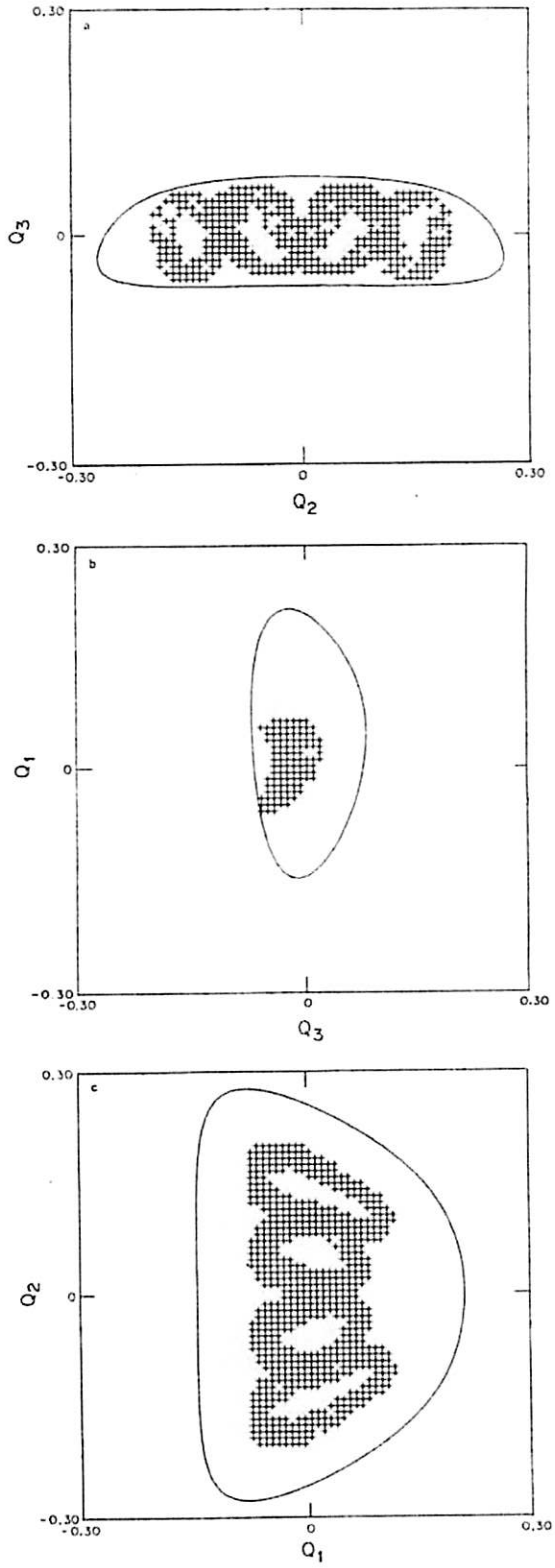

Figure 5. Three views of the $(2,2^0,3)$ state of OCS which show a complicated resonance structure. In Figures 5–8 the initial conditions were determined as described in the caption for Figure 1, except that $E_2 = (n_2 + 1)\omega_2$. Here $E = 11083$.

In Figures 5–7 are plotted trajectories for a model of nonrotating OCS, using the Hamiltonian in ref 12. Each figure provides views of a trajectory in the three planes

(12) A. Foord, J. G. Smith, and D. H. Whiffen, *Mol. Phys.*, 29, 1685 (1975).

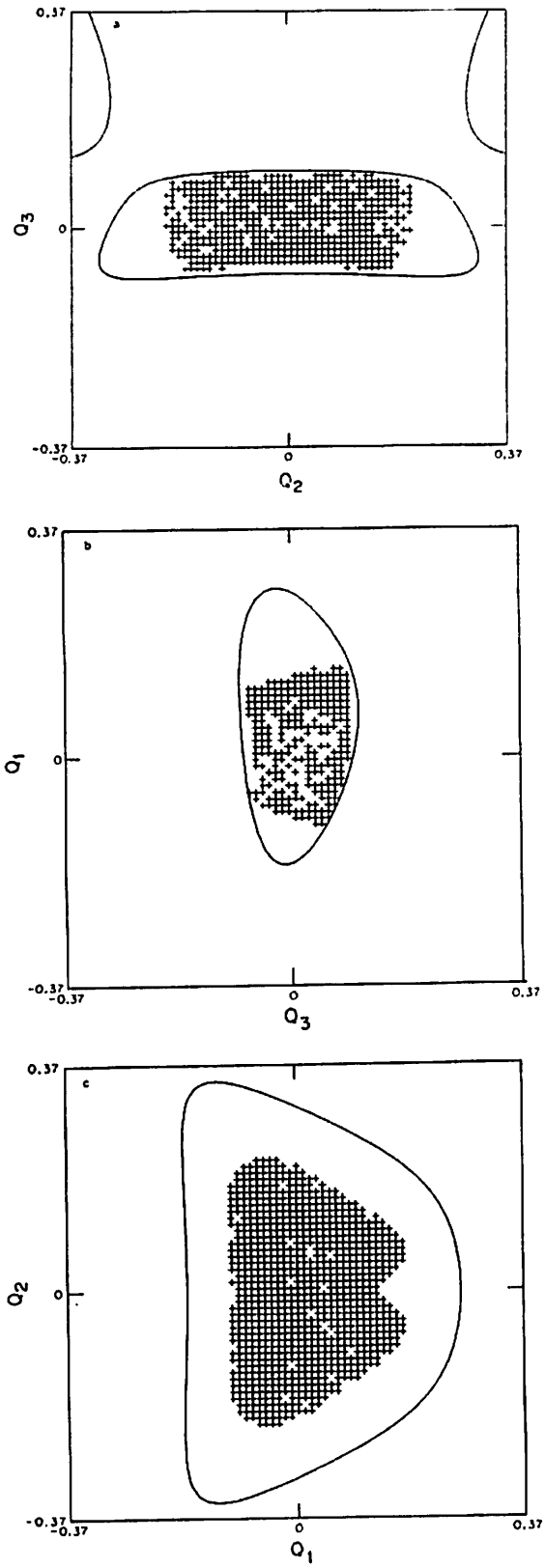

Figure 6. Three views of a quasibound (5,0°,5) state of OCS; E = 16848.

defined by $Q_1 = 0$, $Q_2 = 0$, and $Q_3 = 0$, and labeled a, b, and c, respectively. The solid line is the equipotential contour determined by the total energy.

Figure 5 describes the (2,2°,3) zeroth order state of OCS. The trajectory displays a higher order, accidental 4:1 resonance in the Q_2 and Q_3 degrees of freedom. The 4:1 character of this resonance is demonstrated by the double

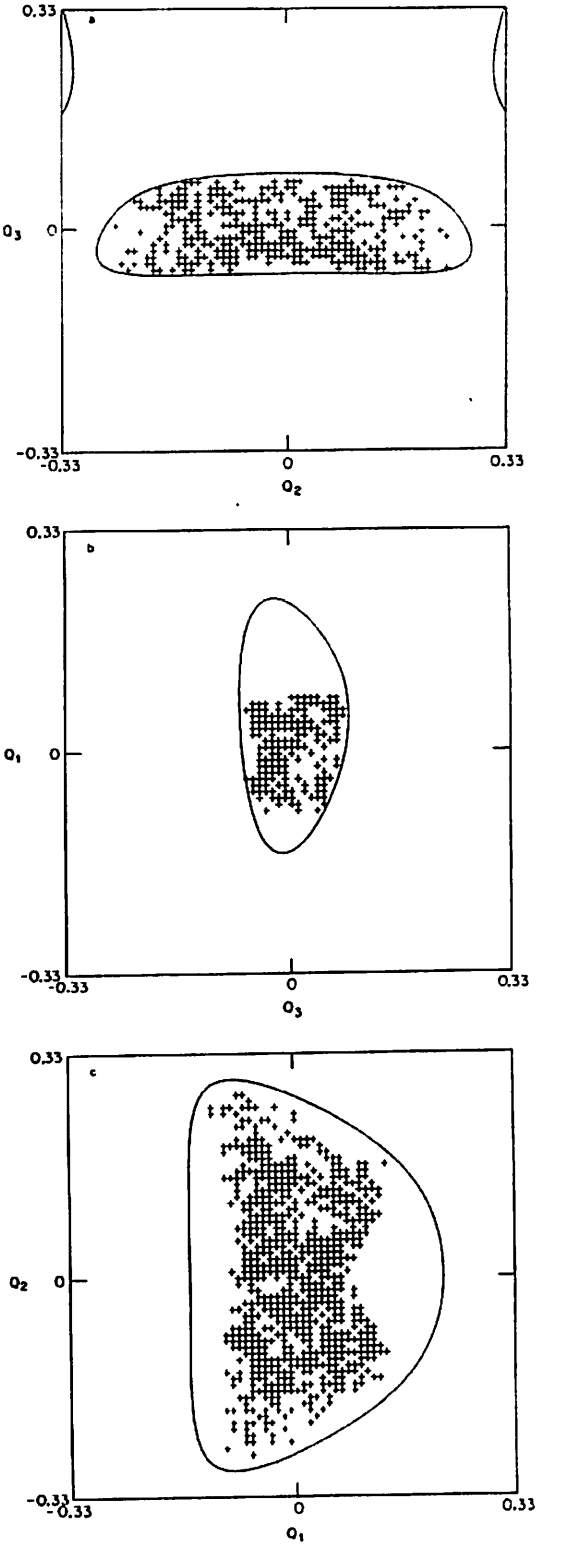

Figure 7. Three views of a "chaotic" trajectory of OCS (state 2,4°,3) at ~180 Q_2 periods; E = 12131.

figure eight pattern of the Q_2–Q_3 cross section (Figure 5a) and the fact that $\omega_3(=1967.0)/\omega_2(=491.7) = 4.00$; the frequencies were obtained from a spectral analysis[13] (Fourier transform) of the coordinates $Q_1(t)$, $Q_2(t)$, and $Q_3(t)$. Although the zeroth order frequencies, $\omega_3^0 = 2092.46$ and $\omega_2^0 = 523.62$, are also close to the ratio 4:1, we note that, for

(13) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *J. Chem. Phys.*, 67, 404 (1977).

most zeroth order OCS states, the addition of the perturbative terms to H_0[12] removes this zeroth order near degeneracy resulting in incommensurate fundamental frequencies and therefore distorted box-type trajectories. (These results are not presented here.) For the $(2,2^0,3)$ state considered here, the initial conditions and the perturbation have combined to restore the 4:1 resonance *accidentally*.

The appearance of four "holes" in the Q_1–Q_3 cross section for this trajectory (Figure 5c), even though the resonance is $\omega_3 \simeq 4\omega_2$ rather than $\omega_3 \simeq 4\omega_1$, is explained as follows: Since the Q_2–Q_3 resonance condition holds for all values of Q_1, we expect the 4:1 pattern, albeit distorted, to persist over a range of Q_1 values. That is, adherence to the condition $\omega_3/\omega_2 = 4.0$ coupled with the incommensurability of ω_1(=817.0) results in excluded *volumes* of configuration space rather than the excluded *areas* associated with resonances in two degrees of freedom systems. Here the excluded volumes can be pictured by orienting Figure 5a at 90° with respect to Figure 5c and lining up the Q_2 axes. Figure 5b simply displays the (solid) Q_1–Q_3 cross section in between the two innermost excluded volumes.

Figure 6 describes a trajectory for the zeroth order $(5,0^0,5)$ state of OCS obtained by using the same Hamiltonian. The trajectory, whose energy exceeds that needed for dissociation, is a quasibound one and is of the distorted box type. This trajectory is the 3-D analogue of a resonance state as found in ref 14.

In Figure 7 are plotted three views of a bound "chaotic" trajectory of OCS at ~180 Q_2 vibrational periods. [The maximum forward time from which this chaotic trajectory could be successfully back integrated[15] was only ~180 Q_2 vibrational periods (~11.7 ps).] The trajectory was detected to be unstable both by its sensitivity to integration error parameters and the associated back integration difficulties, and by its "grassy" power spectrum.[13] We also used the spectral method[13] to show that the trajectories of Figures 5 and 6 were quasiperiodic.

The trajectory plots in Figure 7 are seen to be somewhat similar to those in Figures 5 and 6, but those in Figure 7 appear to be ragged around the edges. We believe that if executed to sufficiently long times the Figure 7 plots might eventually fill up all the classically allowed space. This point was tested by comparing the time evolution of cross sections for a quasiperiodic $(2,0^0,3)$ and a chaotic $(2,4^0,3)$ trajectory to a maximum time of ~1300 Q_2 periods. Despite the onset of numerical integration error, even for the quasiperiodic trajectory, one feature became prominent as time increased. The quasiperiodic cross sections "converged" and retained well-defined boundaries (i.e., the trajectory remained on a torus); a comparison of Figure 8a for ~1300 Q_2 periods and Figure 8b for ~160 Q_2 periods illustrates this feature. In the chaotic case the boundaries remained ragged and the trajectory *slowly* filled the available configuration space (cf. Figure 8c for ~1300 Q_2 periods and Figure 7c for ~180 Q_2 periods). The filling of Figure 7a occurred most rapidly, followed by Figure 7c and then Figure 7b.

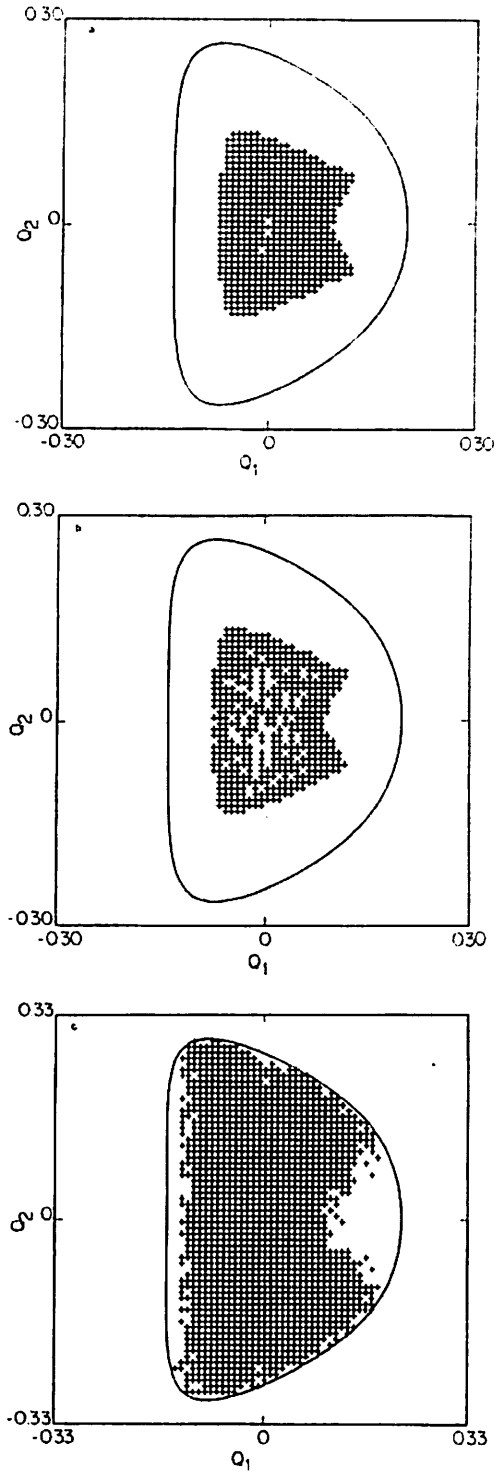

Figure 8. Comparison of the quasiperiodic $(2,0^0,3)$ state of OCS (a) at ~1300 Q_2 periods, (b) at ~160 Q_2 periods, and (c) the chaotic $(2,4^0,3)$ state at ~1300 Q_2 periods; for the $(2,0^0,3)$ state E = 10036.

Conclusions

In this paper, a technique is presented for visualizing both the shape and internal structure of classical trajectories. When this technique is coupled with the surface of section quantization or with perturbation methods which take the observed shape into account, it is possible to quantize essentially all nonrotating triatomic molecules for which quasiperiodic trajectories are found. The advantage of this technique is that the programming effort is trivial. There will be some cases where the trajectories are "chaotic" even if the quantum mechanical states are "regularly spaced".[16] For such trajectories the present

(14) D. W. Noid and M. L. Koszykowski, *Chem. Phys. Lett.*, 73, 114 (1980).

(15) Back integrated in the chaotic case to at least two digits in the coordinates and one digit in the momenta. (The accuracy in the quasiperiodic cases was considerably greater, as was the forward integration time of ~625 Q_2 vibrational periods in Figures 5 and 6.)

(16) D. W. Noid, M. L. Koszykowski, M. Tabor, and R. A. Marcus, *J. Chem. Phys.*, 72, 6169 (1980).

method would, of course, not be useful in the quantization. Another method has been recently developed by Ashton and Muckerman[7] which examines the outer surface of the 3-D classical trajectory.

The two methods are complementary in that Ashton and Muckerman could obtain our results by "slicing" their representation of a trajectory (in the absence of internal resonances) and we could obtain their results by "stacking" our slices. (The stacking was used to obtain Figure 4.)

The resolution of our figures can be altered simply by changing the bin size. In addition, although we have arbitrarily chosen planes perpendicular to the Cartesian axes, *any* slice can be obtained by specifying the associated functional form of G in DEROOT.

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