Semiclassical calculation of eigenvalues for a three-dimensional system

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(Received 7 January 1980; accepted 26 March 1980)

A method utilizing integration along invariant curves on Poincaré's surfaces of section is described for the semiclassical calculation of eigenvalues for three and higher dimensional systems, supplementing thereby our previous work in two dimensions. The eigenvalues calculated for anharmonically coupled oscillators agree well with the exact quantum eigenvalues.

I. INTRODUCTION

The calculation of bound state properties using semiclassical techniques has been of considerable interest for years. The problem has been extensively studied for systems which permit separation of variables. We have recently developed methods for calculating eigenvalues semiclassically for systems which do not permit the separation of variables.[1,2] Other more perturbative semiclassical methods[3] have been developed, and the various methods are complementary.

The path integral method has its origins in Einstein's[4] and old quantum theory and later in WKB-type semiclassical theory.[1,5] The quantum conditions[1,5] for N-dimensional nondegenerate systems are ($\hbar = 1$)

$$2\pi(n_i + \tfrac{1}{2}) = \oint_{C_i} \sum_k p_k dq_k \,, \tag{1.1}$$

where the $\frac{1}{2}$ applies for a system of nondegenerate oscillators; it is replaced by other known values for other systems; the q_k, p_k are coordinates and their conjugate momenta, the n_i the integers, and the C_i are topologically independent closed paths. The closed paths need not actually be along trajectories.

The earliest path-integral method was developed by Eastes and Marcus[2a] for a two-dimensional system. The method involved first the calculation of a single long time trajectory. The caustics (the envelope of the trajectory in coordinate space) were then located; semiclassically the caustics separated the classically allowed from the nonallowed regions. The two independent path integrals for two-dimensional systems were evaluated by integrating along a side of the boxlike caustic. (Evaluation along two adjacent sides sufficed.) This method was successful for trajectories with obvious nonshifting caustics, but would not succeed otherwise.

A more general method was developed[2b-d] in which the independent paths were taken as the Poincaré surfaces of section. The method was applied successfully to a system of two dimensions, both with and without zeroth order resonances, and also to quasibound systems (scattering resonances).[2e] This method also involved the numerical integration of a trajectory, and the behavior of the trajectory in a plane of phase space was examined. Some plane (say $y = 0$) was chosen, and each time the trajectory crossed the plane in a given direction, the point corresponding to the value of x and p_x was marked, thereby generating a closed "curve" of p_x versus x. The same procedure was followed for the $x = 0$ plane where the values of (y, p_y) were noted. These two "surfaces of section" were then used as paths to evaluate the $\int \mathbf{p} \cdot d\mathbf{q}$ integrals. (Curvilinear surfaces of section were used in the resonant cases.) The surface of section can also be used to determine if the motion is quasiperiodic or stochastic. Quasiperiodic motion occurs on a torus in phase space and the surface of section will have a regular pattern. Stochastic motion tends to fill the phase space and the surface of section will have a much more random pattern.

In this paper, the extension of the method to three and higher dimensions is described. The calculation is made more tractable by the introduction of a coordinate transformation from Cartesian coordinates to zeroth order action-angle variables. A sample calculation is made for a three-dimensional nondegenerate system and the agreement with exact quantum-mechanical calculations is excellent.

In Sec. II, the independent paths and the quantum conditions are discussed. The numerical methods and results are shown in Sec. III, and a discussion is presented in Sec. IV.

II. SEMICLASSICAL QUANTIZATION

A three-dimensional oscillator with no resonances is studied here by way of an example. One model Hamiltonian is

$$H = \tfrac{1}{2}[p_x^2 + p_y^2 + p_z^2 + \omega_x^2 x^2 + \omega_y^2 y^2 + \omega_z^2 z^2] + \lambda(xy^2 + \eta x^3) + \mu(yz^2 + \zeta y^3) \,, \tag{2.1}$$

[a] Contribution No. 6018.

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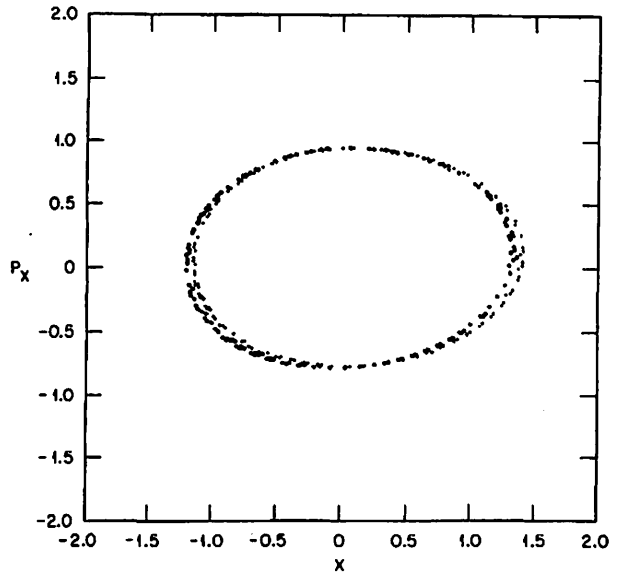

FIG. 1. The p_x vs x surface of section from a particular three-dimensional trajectory ($\epsilon = 0.2$).

where the terms in square brackets describe the uncoupled normal coordinate Hamiltonian for three normal modes. This Hamiltonian serves as one model for a nonrotating nonlinear triatomic molecule having certain anharmonic coupling terms between several normal modes. The parameters used for the calculation are $\omega_x^2 = 0.49$, $\omega_y^2 = 1.69$, $\omega_z^2 = 1.00$, $\lambda = \mu = -0.10$, and $\eta = \zeta = 0.10$. The Hamiltonian from Eq. (2.1) yields trajectories which are the three-dimensional analogs to the "boxlike" trajectories of two dimensions and are thereby "cube" type.

The behavior of solutions to Eq. (2.1) is next examined in phase space so as to calculate the three independent path integrals needed to obtain the energy eigenvalues. First, the (x, p_x) plane is examined, wherein points with $y = z = 0$ are collected. The semiclassical wave function has 2^3 branches for this boxlike, three-dimensional system (all possible permutations of $p_x \gtrless 0$, $p_y \gtrless 0$, $p_z \gtrless 0$). The branch chosen in Fig. 1 has $p_z \geq 0$ and $p_y \geq 0$. The corresponding surface of section, plotted in Fig. 1, can be seen to form a well-defined closed path, just as did the two-dimensional surfaces of section of Ref. 2(a). The quantum condition for this path is (in units of $\hbar = 1$)[1,5]

$$\oint_{C_1} \mathbf{p} \cdot d\mathbf{q} \equiv \oint_{C_1} p_x dx = 2\pi(n_1 + \tfrac{1}{2})$$
$$(y = 0,\ z = 0 \text{ surface of section}). \qquad (2.2)$$

The first equality in Eq. (2.2) results because $dy = dz = 0$ along the path C_1.

Similarly, one has

$$\oint_{C_2} \mathbf{p} \cdot d\mathbf{q} \equiv \oint_{C_2} p_y dy = 2\pi(n_2 + \tfrac{1}{2}) , \qquad (2.3)$$

$$\oint_{C_3} \mathbf{p} \cdot d\mathbf{q} = \oint_{C_3} p_z dy = 2\pi(n_3 + \tfrac{1}{2}) . \qquad (2.4)$$

Another quantization condition which incorporates (2.2)–(2.4) is

$$\oint_{\substack{\text{closed} \\ \text{path}}} \sum_i p_i dq_i = 2\pi(N + \tfrac{1}{2} l) , \qquad (2.5)$$

where $2l$ is the number of times the path touches a caustic. N is an integer. Equation (2.5) is used later to increase the accuracy of eigenvalues calculated from (2.2)–(2.4).

III. RESULTS

Hamilton's equations for the Hamiltonian (2.1) were integrated using the program DEROOT[6] (Sandia National Laboratories). Beside integrating the trajectory, this program automatically determines points on the trajectory which are the roots of an equation provided by the user. The root-searching part of DEROOT was set to return points when the equation

$$xyz = 0 \qquad (3.1)$$

was satisfied. These points were saved for later use in evaluating the surface of section. For example, consider the (x, p_x) plane. The points which solve Eq. (3.1) were searched for $y = 0$. Now, we technically need $z = 0$ also to calculate a p_x vs x surface of section, but these $x = 0$ and $z = 0$ conditions occur simultaneously so infrequently that instead the points with $|z| \leq \epsilon$ (where ϵ is some small number) were collected. Of these points those with positive p_y and positive p_z were selected and plotted as p_x versus x. Figures 1–3 each have some "width" to the invariant curve because ϵ was not negligibly small. Figure 4 is intended to show schematically which set of points in coordinate space was collected, where the thickness of the rectangles enclosing the axis is $\frac{1}{2}\epsilon$. The smaller ϵ is, the smaller the thickness. A similar procedure was followed for the other surfaces of section, as in Figs. 2 and 3. Table I summarizes the conditions used to determine the three surfaces of section.

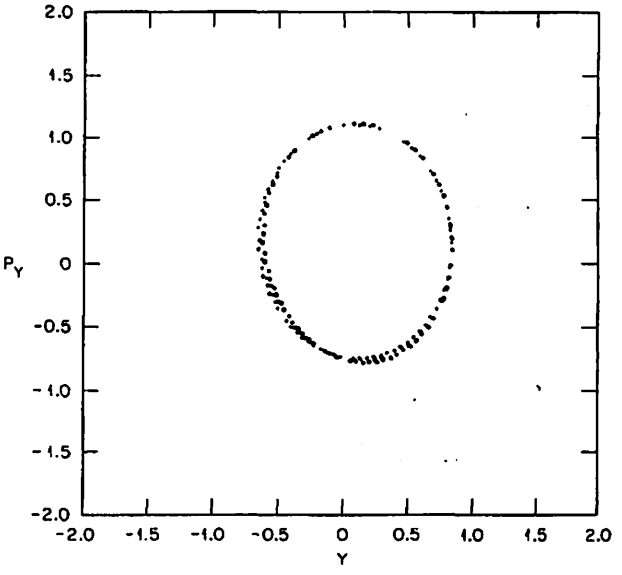

FIG. 2. The p_y vs y surface of section for the same trajectory as that in Fig. 1.

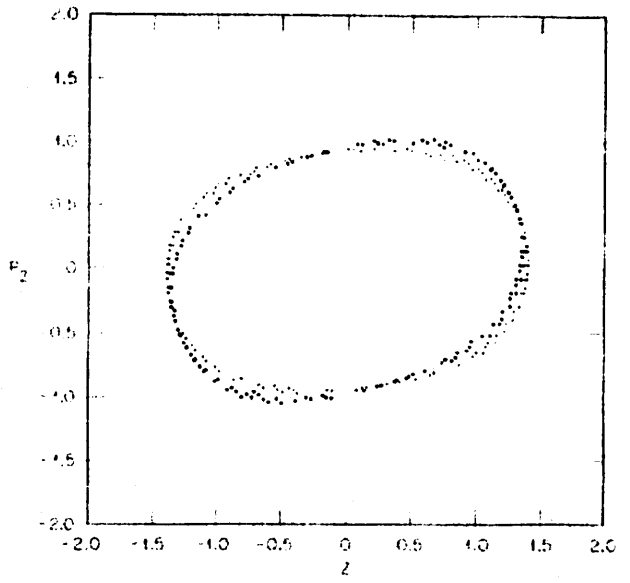

FIG. 3. The p_z vs z surface of section for the same trajectory as that in Fig. 1.

The surface of sections were next transformed from Cartesian coordinates to zeroth order action-angle variables to facilitate the numerical integration. In this action-angle space the surfaces of section are "lines" rather than "ellipses" and fewer points are required to accurately evaluate the $\int \mathbf{p} \cdot d\mathbf{q}$ integrals.

Indeed, because of the "width" the numerical integration performed on the Cartesian p_q vs q data would make it difficult to correctly order the points as well as to obtain stable converged values for the integrals. This difficulty was removed, however, by the present canonical transformation to the line. The width of the line in the new coordinates averages to zero when the area is evaluated. This transformation is indeed a key step in the present evaluation.

These action-angle variables used are the zeroth order ones, i.e., those associated with the normal coordinate Hamiltonian, and so the action variables will not be constants but will vary slightly along the trajectory. The transformation from Cartesian coordinates (q_i, p_i) to action-angle variables[7] (J_i, w_i) is given by (3.2) with a standard convention on the relation between the phase w_i and the sign of p_i:

$$2\pi w_i = \tan^{-1}(\omega_i q_i / p_i) , \tag{3.2}$$

and

$$J_i = \pi(p_i^2 + \omega_i^2 q_i^2)/\omega_i , \tag{3.3}$$

where ω_i is the zeroth order angular frequency of the ith coordinate. A transformed surface of section is shown in Fig. 5. The width of the line is again due to

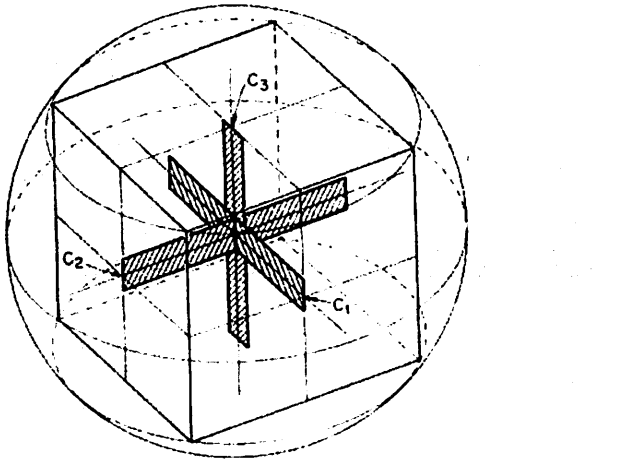

FIG. 4. The rectangles on the axis are the regions in coordinate space used to obtain the points on the surfaces of section.

TABLE I. Determination of surface of sections.

Plane	Path	x	y	z	p_x	p_y	p_z
(x, p_x)	C_1	x	0	$\leq \epsilon^b$	p_x	≥ 0	≥ 0
(y, p_y)	C_2	$\leq \epsilon^b$	y	0	≥ 0	p_y	≥ 0
(z, p_z)	C_3	0	$\leq \epsilon^b$	z	≥ 0	≥ 0	p_z

[a]See Fig. 6. [b]I.e., $|z| \leq \epsilon$, or $|x| \leq \epsilon$, or $|y| \leq \epsilon$.

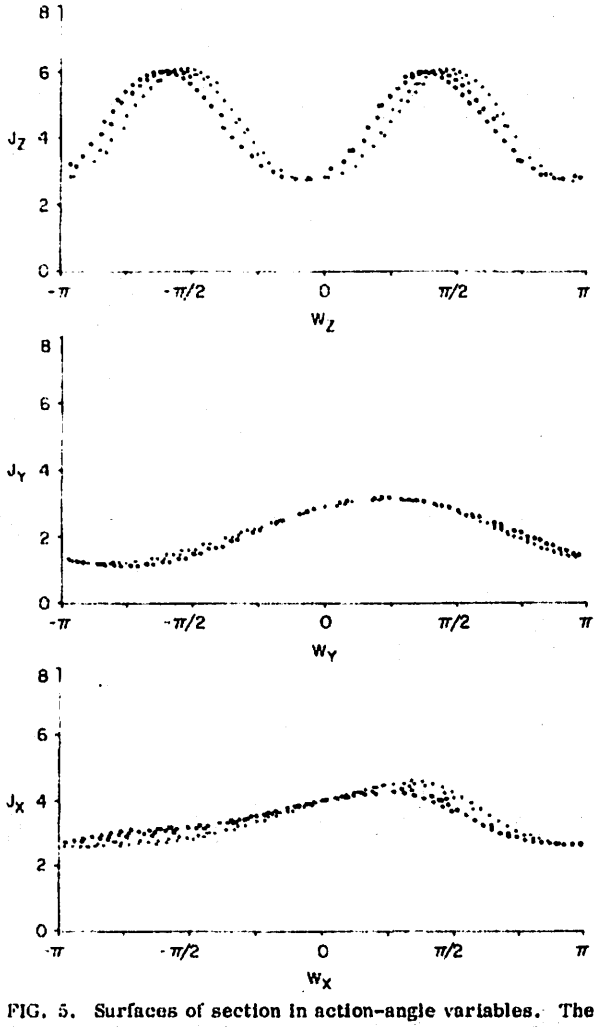

FIG. 5. Surfaces of section in action-angle variables. The pluses are for $q > 0$ and $|q| < \epsilon$, while the circles are for $q < 0$ and $|q| < \epsilon$.

TABLE II. Comparison of quantum and semiclassical eigenvalues.

State[a]	$E_{quantum}$	E_{semi}	E^0
0,0,0	1.494	1.493	1.500
1,0,0	2.185	2.184	2.200
0,0,1	2.486	2.485	2.500
0,1,0	2.771	2.771	2.800
2,0,0	2.873	2.872	2.900
1,0,1	3.177	3.177	3.200

[a]Values of (n_1, n_2, n_3).

the finite value of ϵ from Table I, and the + corresponds to having q in the range $|q| \leq \epsilon$ be a positive number, while the circles correspond to $[q \leq 0, |q| \leq \epsilon]$. The path integrals in Eqs. (2.2)–(2.4) now become

$$\int_0^1 J_i dw_i = 2\pi(n_i + \tfrac{1}{2}) \quad (i = 1, 2, 3) . \tag{3.4}$$

When Eq. (3.4) is evaluated, the width of the surface of section is effectively averaged and the correct average value of the path integral is obtained. The value of the integral has been shown (numerically in the present study) to be independent of ϵ for small ϵ.[8] The numerical results of using this procedure on the Hamiltonian (2.1) are presented in Table II.

A linear interpolation was used to find the eigentrajectory for which n_1, n_2, and n_3 all equal the desired integers. The interpolation equations used, analogous to those discussed in Ref. 2(a), were

$$\begin{aligned} n_1 &= A_1E_x + B_1E_y + C_1E_z + D_1 , \\ n_2 &= A_2E_x + B_2E_y + C_2E_z + D_2 , \\ n_3 &= A_3E_x + B_3E_y + C_3E_z + D_3 , \end{aligned} \tag{3.5}$$

where

$$E_x = F_xE, \quad E_y = F_yE, \quad E_z = E - E_x - E_y .$$

F_x and F_y refer to the zeroth order fraction of the total energy initially put into the x and y coordinates, i.e., $(p_x^2 + \omega_x^2x^2)/2E$ and $(p_y^2 + \omega_y^2y^2)/2E$, respectively. The constants were evaluated using four trajectories, the eigentrajectory was interpolated and the procedure was iterated with several more trajectories to test convergence.

To obtain better convergence and accuracy this eigentrajectory (E, F_x, F_y) was used to calculate the total phase with the trajectory close method of Ref. 2(b), i.e., i.e., the total phase $\phi(t)$ was computed by integrating the additional equation

$$d\phi/dt = \sum_i p_i dq_i/dt \tag{3.6}$$

and connecting with the trajectory at $t = 0$ on a surface of section. The procedure was iterated by changing E and finding the E for which, with ϕ calculated over the closed path, one has

$$\phi = 2\pi N + l\pi. \tag{3.7}$$

In this two-step approach E was only varied by 0.005 in the second step. With this method for checking the phase consistency the accuracy for the eigenvalues was enhanced an order of magnitude. The principal idea underlying it is that E depends more on the principal quantum number (related to N) than on n_1, n_2, and n_3. Thus, it suffices to have n_1, n_2, and n_3 close to integers but to have N even closer to an integer.

The quantum mechanical eigenvalues were computed using the variational method and a large basis set. A product wave function

$$\psi = \sum\sum\sum \psi_i(x)\psi_j(y)\psi_k(z) \tag{3.8}$$

was used where $\psi_i(x)$, $\psi_j(y)$, and $\psi_k(z)$ are harmonic oscillator wave functions and are solutions to the equation

$$H^0\psi = E^0\psi , \tag{3.9}$$

where H^0 is the term in brackets for (2.1). The Hamiltonian matrix was diagonalized using the program EISPAC.[9]

The semiclassical and quantum results for the eigenvalues are given in Table II.

IV. DISCUSSION

The semiclassical method outlined in this paper is seen to provide accurate eigenvalues for the Hamiltonian (2.1) (Table II). It is more economical than a quantum mechanical variational calculation, when the matrix elements used in the latter must be integrated numerically (rather than available analytically) and when, at the same time, only a few eigenvalues are desired. The present procedure can be extended to both zeroth order and exact degenerate systems. Combined with the techniques of Ref. 2(b)–2(d), it enables semiclassical eigenvalues to be calculated for a general N-dimensional Hamiltonian with and without degeneracies.

The method outlined here succeeds for Hamiltonians whose trajectories are quasiperiodic for the energies of interest. A quasiperiodic trajectory has a regular pattern in the surface of secion. At higher energies, the patterns on the surface of sections become random, first near the separatrices (lines separating resonance centers) and then at higher energies everywhere. At these higher energies, a typical surface of section will have resonance centers and a stochastic "shotgun" pattern. The trajectories associated with the random patterns are stochastic, and in coordinate space they "randomly" fill the classically accessible coordinate space. It has also been found that the frequency spectrum of this motion no longer consists of sharp lines, but becomes a band.[11–13] The stochastic trajectories of a N-dimensional system apparently do not have N isolating integrals of the motion, the total energy being the only isolating integral. Accordingly, they cannot be quantized with the present method.

ACKNOWLEDGMENTS

One of us (D.W.N.) was supported by a Wigner Fellowship from ORNL. The research was sponsored by the U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corp. (at Oak Ridge), the National Science Foundation (at the University of Illinois and at California Institute of Technology), and the DOE

(at Sandia, Livermore). We also wish to thank Mrs. Mary Ann Berg at the University of Illinois for helpful discussions on numerical techniques.

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