

INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the original submitted.

The following explanation of techniques is provided to help you understand markings or patterns which may appear on this reproduction.

1. The sign or "target" for pages apparently lacking from the document photographed is "Missing Page(s)". If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting thru an image and duplicating adjacent pages to insure you complete continuity.
2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.
3. When a map, drawing or chart, etc., was part of the material being photographed the photographer followed a definite method in "sectioning" the material. It is customary to begin photoing at the upper left hand corner of a large sheet and to continue photoing from left to right in equal sections with a small overlap. If necessary, sectioning is continued again - beginning below the first row and continuing on until complete.
4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from "photographs" if essential to the understanding of the dissertation. Silver prints of "photographs" may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.
5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

University Microfilms International

300 North Zeeb Road
Ann Arbor, Michigan 48106 USA
St. John's Road, Tyler's Green
High Wycombe, Bucks, England HP10 8HR

7904276

SWINN, RANDALL THOMAS
SEMICLASSICAL CALCULATION OF VIBRATIONAL
ENERGY LEVELS FOR NONSEPARABLE SYSTEMS.

THE COLLEGE OF WILLIAM AND MARY IN VIRGINIA,
PH.D., 1970

University
Microfilms
International

300 N. ZEEB ROAD, ANN ARBOR, MI 48106

SEMICLASSICAL CALCULATION OF VIBRATIONAL ENERGY LEVELS
FOR NONSEPARABLE SYSTEMS

A Dissertation
Presented to
The Faculty of the Department of Physics
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Doctor of Philosophy

by
Randall Thomas Swimm
August 1978

APPROVAL SHEET

This dissertation is submitted in partial fulfillment of
the requirements for the degree of

Doctor of Philosophy

Randall T. Swimm
Randall Thomas Swimm

Approved, July 1978

John B. Delos
John B. Delos

Hans C. von Baeyer
Hans C. von Baeyer

Arden Sher
Arden Sher

John R. Kane
John R. Kane

Donald W. Noid
Donald W. Noid
Oak Ridge National Laboratory

TABLE OF CONTENTS

	Page
ACKNOWLEDGMENTS	v
LIST OF TABLES	vi
LIST OF FIGURES	vii
ABSTRACT	viii
I. INTRODUCTION	2
Reader's Guide	5
II. FOUNDATIONS AND HISTORICAL BACKGROUND	6
A. Quasiperiodic and Ergodic Motion in Classical Mechanics	6
1. Separable Classical Systems	8
2. Nonseparable Classical Systems	17
B. The Nature of Quantum States	24
C. Semiclassical Methods for the Quasiperiodic Case	29
1. Review of One-Dimensional WKB Method	30
2. Multidimensional Semiclassical Quantization	39
3. Computational Methods	47
a. Numerical Trajectory Calculations	48
b. Method for Transformation to Angle-Action Variables	57
c. Quantization for Irregular Classical Orbits	63
d. Calculation of Invariant Toroids	64

III.	THE BIRKHOFF-GUSTAVSON NORMAL FORM	68
	Transformation to Normal Form	70
IV.	QUANTIZING THE NORMAL FORM	85
	A. The Incommensurable Case	86
	B. The Commensurable Case	94
V.	CONCLUSION	109
	A. Summary	109
	B. Comparisons	110
	C. Extensions and Limitations	115
	D. Applications	117
	Appendix I. Review of Hamilton-Jacobi Theory	119
	Appendix II. Energy Levels for Symmetric One-Dimensional Double Well	126
	Appendix III. Semiclassical Solution of the Schrödinger Equation	131
	Appendix IV. Example for Calculation of Normal Form	138
	REFERENCES	141

ACKNOWLEDGMENTS

I wish to thank the following persons: my advisor John Delos for the great time and effort he has contributed to this work;

John Kane and Arden Sher for serving on my thesis committee;

Hans von Baeyer for his frequent help and cooperation during his term as chairman, and for serving on my thesis committee;

Don Noid for generously performing many computer computations used in this research, and for serving on my thesis committee;

Carl Andersen for his assistance during the writing of the MACSYMA programs used for our calculations.

I am especially grateful to Ed Reuler for his encouragement and for sharing his thoughts with me.

I wish to thank Sylvia Stout for her dedication above and beyond the call of duty during my time at William and Mary.

Finally, I wish to thank my wife, Kathy, for being there when I needed her.

LIST OF TABLES

Table		Page
IV.2	Energy Levels for an Incommensurable Case	89
IV.2	Energy Levels for a Commensurable Case	102

LIST OF FIGURES

Figure		Page
II.1a	Quasiperiodic Trajectory	7
II.1b	"Ergodic" Trajectory	7
II.2	Trajectory in Angle-Variable Space	11
II.3	Visual Aid	16
II.4	Surface of Section at Low Energy	20
II.5	Surface of Section at High Energy	21
II.6	One-Dimensional Single Well	35
II.7	One-Dimensional Double Well	38
II.8	Integration Paths in Configuration Space	41
II.9	Integration Paths in Phase Space	43
II.10	Libration Trajectory	51
II.11	Rotation Trajectory	51
II.12	Trajectories for the Unperturbed System	53
IV.1	Rotation Trajectory	96
IV.2	Libration Trajectory	97
IV.3	Roots for a Rotation Case	99
IV.4	Roots for a Libration Case	99
V.1	Schematic Comparison	112
A2.1	One-Dimensional Double Well	126
A3.1	Trajectories Turning at a Caustic	132

ABSTRACT

We present a semiclassical method of calculating vibrational energy levels for a system of nonseparable coupled oscillators. For a Hamiltonian written as a power series in which the leading terms are given by a sum of one-dimensional harmonic oscillator Hamiltonians representing an unperturbed limit of the full Hamiltonian, the method involves transforming the original classical Hamiltonian via a succession of canonical transformations into a normal form, which is a power series originally defined by Birkhoff and later generalized by Gustavson. Two cases are distinguished. If the harmonic oscillator frequencies in the unperturbed Hamiltonian are incommensurable then the normal form is a power series whose terms are products of one-dimensional harmonic oscillator Hamiltonians; if the frequencies in the unperturbed Hamiltonian are commensurable then additional terms which cannot be written as products of one-dimensional harmonic oscillator Hamiltonians enter into the normal form. Once the normal form is obtained, semiclassical quantization of action variables is straightforward. The incommensurable case yields a formula for the energy spectrum which is a power series in the quantum numbers. The commensurable case is more complicated, and yields a form from which energy levels may be obtained individually by numerical calculation and quantization of a one-dimensional phase integral. Nonseparable two-dimensional examples are treated for each case. The results obtained for both cases show excellent agreement with quantum mechanical calculations.

SEMICLASSICAL CALCULATION OF VIBRATIONAL ENERGY LEVELS
FOR NONSEPARABLE SYSTEMS

I. INTRODUCTION

This thesis presents a semiclassical method of calculating the vibrational energy levels of a system of nonseparable coupled oscillators such as might be encountered in the study of vibrational energy levels of polyatomic molecules. The semiclassical method has long been recognized as a powerful method of finding approximate solutions to the Schrödinger equation. However, until recently the semiclassical method has been applied primarily to one-dimensional systems, or to separable multidimensional systems which may be written as a set of uncoupled one-dimensional systems. Recently Marcus¹ and others²⁻⁶ have developed techniques for treating non-separable bound systems using semiclassical methods. Unfortunately, these techniques are somewhat cumbersome to apply since they require a fairly lengthy iterative numerical calculation to be made in order to obtain each energy level. One of the main motivations for this research was to provide an efficient analytical method for treating nonseparable systems using semiclassical methods. By carrying out the calculation analytically, it has been possible in some cases to obtain the entire energy spectrum with roughly the same effort that numerical methods require in order to obtain a single energy level.

Semiclassical methods of calculating bound state eigenvalues require two steps. First the classical equations of motion must be

solved, and then the classical solutions must be quantized. We therefore begin by presenting a detailed description of the nature of the classical systems which we are studying. It happens that nonseparable classical systems can display a behavior which is amazingly different from that of separable systems. We first review the behavior of separable classical systems, in order to establish traditional concepts, and then we discuss the behavior of nonseparable systems, and show how it differs from that of separable systems.

After treating classical systems, we discuss semiclassical quantization methods. As mentioned earlier, one-dimensional methods are well established, and we therefore begin by considering these. We then describe current methods of treating nonseparable systems semiclassically, and show how the one-dimensional concepts must be generalized.

After we have reviewed the nature of nonseparable classical systems, and discussed the general theory of semiclassical quantization, we then present the specific method that we have developed. Again this must be done in two steps. We begin by describing the method which we use to provide the solution to the classical equations of motion. This method was developed fifty years ago by Birkhoff,⁷ and more recently generalized by Gustavson.⁸ In order to apply this method, the classical Hamiltonian must be written as a power series in which the leading terms are given by a sum of one-dimensional harmonic oscillator Hamiltonians representing an unperturbed limit of the full Hamiltonian. Birkhoff's original method applies if the harmonic oscillator frequencies which

appear in the unperturbed Hamiltonian are incommensurable (i.e. their ratios are not rational numbers). In that case he showed that the Hamiltonian could be transformed into a normal form which is a power series whose terms are products of one-dimensional harmonic oscillator Hamiltonians. If any commensurability relations exist among the harmonic oscillator frequencies which appear in the unperturbed Hamiltonian, then Gustavson's generalization of Birkhoff's original method applies. In this case additional terms which cannot be written as products of one-dimensional harmonic oscillator Hamiltonians appear in the normal form.

Once we have presented Birkhoff's method of solving the classical equations of motion, we proceed to quantize the normal form using the semiclassical prescription. In the incommensurable case we obtain a formula which provides the energy spectrum in the form of a power series in the quantum numbers. In the commensurable case, we obtain a form from which energy levels can be obtained individually by satisfying a semiclassical quantization condition numerically. Specific two-dimensional examples are treated for both incommensurable and commensurable cases. In an incommensurable case we obtain 83 energy levels up to the escape energy with excellent accuracy. In a commensurable case we obtain 42 energy levels (the highest of which is within 2% of the escape energy), which while not so accurate as the results for the incommensurable case, do verify the applicability of our semiclassical method for the commensurable case.

Reader's Guide

Chapter II provides a general background and foundation for our work, and contains three sections. The first section reviews the classical behavior of systems of interest. The second section contains a discussion of the nature of quantum mechanical systems and attempts to show how the nature of the classical system might be reflected in the quantum mechanical behavior. The third section reviews current semiclassical methods for obtaining eigenvalues of a bound system.

Chapter III contains all of the classical considerations which are directly related to our semiclassical quantization method. The Birkhoff-Gustavson normal form is derived, and the classical form is presented for two-dimensional examples of both the incommensurable and commensurable cases. It is shown that the normal form for the incommensurable case may be expressed completely in terms of action variables, while the normal form for the commensurable case may be expressed in terms of one action variable and a canonical coordinate and momentum.

Chapter IV contains a description of the method used to quantize the normal form. Also shown are the quantized results for the two examples treated in Chapter III.

Chapter V is the conclusion. In this chapter the major ideas involved in our method are summarized, and limitations and possible extensions of our method are discussed. Our method is compared to recent numerical semiclassical methods for treating nonseparable systems, and to quantum mechanical methods. Possible applications of our methods are discussed. Finally, indirect contributions of our work are discussed.

II. FOUNDATIONS AND HISTORICAL BACKGROUND

A. Quasiperiodic and Ergodic Motion in Classical Mechanics

Let us consider the classical behavior of nonseparable multi-dimensional oscillators. The work presented here deals primarily with two degrees of freedom, and therefore forms a basic model for the longitudinal vibrations of a linear triatomic molecule. The method should also be applicable to systems of more than two degrees of freedom.

As this thesis will discuss, the motion for a system of coupled oscillators can be very complicated. In order to illustrate this, Fig. II-1a,b show examples of motion for a system of two degrees of freedom. The figures show the trajectory generated by a point moving on a potential surface. The axes may be taken to represent the x-y coordinates of the point as it moves in a two-dimensional well, or equivalently as the amplitudes of the symmetric and antisymmetric stretch of a linear triatomic molecule. As is clearly evident, two distinct types of behavior appear.

In Fig. II-1a is a plot of a typical trajectory having a small amplitude of vibration; this trajectory forms a somewhat distorted Lissajous figure. Notice that adjacent segments of the trajectory form an orderly family. The motion is confined to a box-like region, and will not fill the entire energetically allowed region; only the corners of the box touch the energy boundary. This motion is called quasiperiodic.

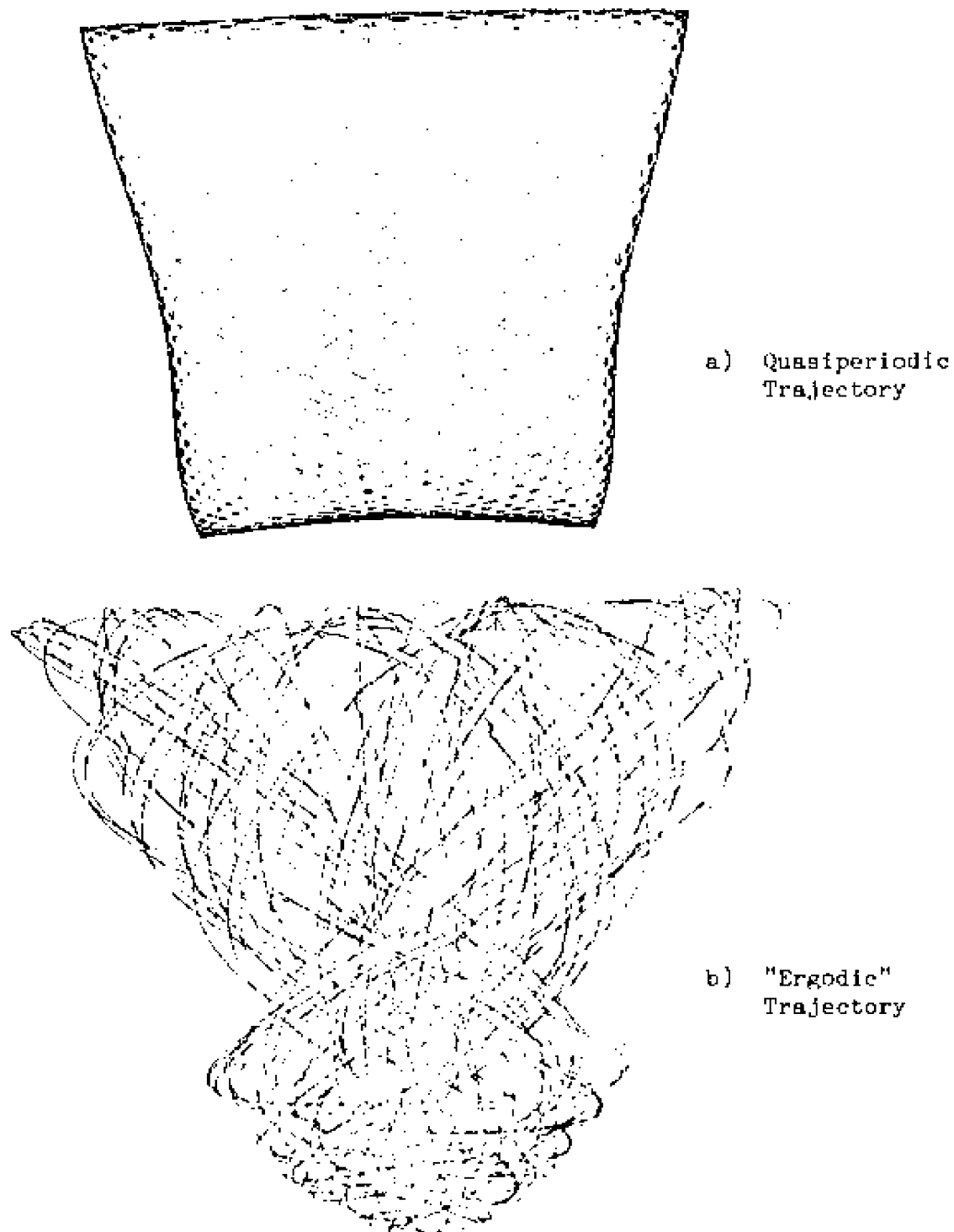


Fig. II.1. Typical trajectories for a two-dimensional Morse potential.

In Fig. II-1b is a typical trajectory having a large amplitude of vibration (the scales of these two figures are different). The motion, though still deterministic, is much less orderly, and no regular pattern is evident. After sufficient time, the motion will fill the energetically allowed region. This motion is commonly referred to as ergodic, although as will be discussed later, this term is somewhat loosely applied. The important point for now is that the motion is rather chaotic in appearance.

The remainder of this section is devoted to a discussion of the classical behavior of systems of coupled oscillators. The concepts involved are first illustrated by considering separable systems (which are exclusively quasiperiodic). Nonseparable systems are then discussed, using an understanding of the separable system as a guide. Only after the classical mechanical nature of the nonseparable system is displayed can the considerations involved in applying semiclassical quantization methods be understood.

1. Separable Classical Systems

Most of the concepts required to treat nonseparable multi-dimensional systems are generalizations of methods used for separable systems. In order to develop these ideas, we begin by treating a separable system using Hamilton-Jacobi theory (hereafter referred to as H-J theory). The reader is referred to Appendix I for a review of H-J theory; only the relevant results are repeated here.

We begin by considering a system described by a time independent Hamiltonian $H(q,p)$, where q are coordinates, p are momenta, and (q,p) is a shorthand notation for $(q_1, \dots, q_n, p_1, \dots, p_n)$. We would like to solve the time independent H-J equation

$$H\left(q, \frac{\partial W}{\partial q}\right) - \alpha_1 = 0 \quad (\text{II.1})$$

(where W is a type-2 generating function⁹ and α_1 is the energy) to obtain a generating function which will allow a canonical transformation from the original variables (q,p) to new variables (Q,P) such that the new canonical momenta P are constant as a function of time. If the nature of the system is such that the generating function W may be written as a separable sum

$$W = \sum_i W_i(q_i, P_1, \dots, P_n) \quad (\text{II.2})$$

then the H-J equation may be solved in a straightforward manner. For separable bound problems, all motion is of the class shown in Fig. II-1a - namely quasiperiodic. For such systems, it is possible to choose the angle-action variables (w,J) as the new canonical coordinates and momenta. This is a particularly useful choice.

The action variables J may be defined by

$$J_i = \oint p_i dq_i \quad (\text{no sum}) \quad (\text{II.3})$$

(no sum)

where the integral is taken over one cycle of motion for the coordinate q_1 , with all other coordinates either held fixed, or if allowed to vary, then returned to their original values without having passed through a full cycle. The integral in the definition of the action variable is often referred to as the phase integral; its path independence is ensured here by the separable form of W .

The angle variables w increase linearly with time:

$$\dot{w}_i = \nu_i (J_1, \dots, J_n) \quad (II.4)$$

where ν_i is a constant since the J are constant. The angle variables have the further property that if the original coordinate q_1 passes through one cycle, with all other coordinates either held fixed, or allowed to vary, but being brought back to their original values without having passed through a full cycle, then the angle variable w_i will change by the amount $\Delta^{(j)} w_i$ given by

$$\Delta^{(j)} w_i = \delta_{ij} \quad (II.5)$$

In other words, w_i will increase by unity if q_1 passes through one cycle (with other coordinates restricted as above), but will be unchanged after q_j ($j \neq 1$) passes through one cycle. (This completes the information repeated from Appendix I.)

This property of w is used to provide a mathematical definition of the term quasiperiodic, which has been used only in an intuitive fashion up to this point. Consider the coordinates $q(w_1, \dots, w_n)$, and let w_k increase by 1, holding the other w 's fixed. q_k will go through one cycle; the other q 's may also depend on w_k , but they return to their initial values without passing through a complete cycle (otherwise other w 's would also increase by one). We may therefore express the q_k in terms of a Fourier series in the w 's

$$q_k = \sum_{j_1, \dots, j_n} a_{j_1, \dots, j_n}^{(k)} e^{2\pi i (j_1 w_1 + \dots + j_n w_n)} \quad (\text{II.6})$$

Motion for which the coordinates may be expressed in terms of a convergent Fourier series with a finite number of basic frequencies is called quasiperiodic.^{10a}

In order to illustrate another property of this type of motion, for which action and angle variables may be defined, consider a two-dimensional case for the moment. If we plot the trajectory in w -space, we obtain the diagram of Fig. II.2.

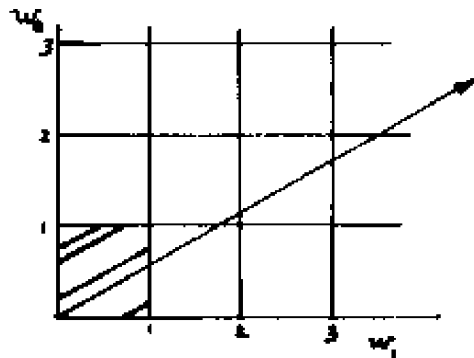


Fig. II.2

Trajectory in Angle-Variable Space

Using the property that w_1 increases by one when q_1 passes through one cycle, we can divide the w_1, w_2 space into unit cells in which congruent points correspond to the same point in phase space.

We can follow a trajectory as w_1 and w_2 increase linearly with time. Since the cells are all equivalent, we can concentrate on a single cell and transfer the segment of the trajectory in any other cell back to the congruent segment in the standard cell. Notice that the slope of the trajectory is ω_2/ω_1 . If this ratio is rational, the trajectory will ultimately be mapped onto itself, and the motion will be periodic. If the ratio is irrational, the trajectory will fill the standard cell densely, and will not be periodic.

The property that congruent points in every cell correspond to equivalent points in phase space, and the consequent property that all motion can be mapped back onto a single cell shows that the motion is topologically equivalent to flow on a torus.¹¹ $2\pi w_i$ can be thought of as an angle variable on the torus. In the two degree of freedom example shown here, there are two angle variables, and consequently a two-dimensional toroidal surface; in the case of n degrees of freedom there will be n angle variables, and the motion will be a flow on an n -torus. This torus is sometimes referred to as an invariant torus^{10a,c,12} because the trajectory always remains on the torus. Recalling that as the coordinate q_1 passes through one cycle, the angle variable w_1 increases by one, we see that evaluating the phase integral (II.3) corresponds to integrating around the invariant torus. There are n independent phase integrals, and n topologically independent paths around an n -torus.

The parallel segments of the trajectory which are plotted on the unit cell (Fig. II.2) will form a family. This family is called a manifold, and is in analogy to streamlines as defined in hydrodynamic theory, or rays as defined in geometrical optics. Such a manifold will also be found on the invariant torus; as the trajectory winds around the surface, it will ultimately either fill the surface with parallel threads (irrational frequency ratio ν_2/ν_1) or will close on itself (rational frequency ratio). The orderly nature of the manifold will also be seen if the n-torus is mapped onto configuration space. This effect is evident in Fig. II.1a.

One additional concept must be introduced - that of an isolating integral.¹³ In general, there exist $2n-1$ independent functions which are constant along a trajectory generated in $2n$ -dimensional phase space. These functions are called integrals of the motion, or simply integrals. In effect, we may think of the integrals as defining surfaces whose intersection defines the trajectory of the system point in phase space.

It may happen that the trajectory does not have access to a full $2n$ -dimensional region of phase space. For example, if the energy is conserved, then the trajectory is constrained to remain on the "energy shell" in phase space - a $(2n-1)$ -dimensional surface in n -dimensional phase space. If the energy is given by the Hamiltonian, then this Hamiltonian may be chosen as one of the integrals of the motion, since its value is constant along the trajectory. Such an integral, which

causes the trajectory to be restricted to a region of phase space reduced in dimension by one is referred to as an isolating integral. An integral which does not so restrict the trajectory is referred to as a non-isolating integral. Only isolating integrals are of physical interest, and are usually simply referred to as integrals.

As an example of a system which possesses more than one isolating integral, consider a two-dimensional harmonic oscillator. This is equivalent to a system of two uncoupled harmonic oscillators. The Hamiltonian for such a system is

$$H = \frac{P_x^2}{2m} + \frac{1}{2} m \omega_x^2 X^2 + \frac{P_y^2}{2m} + \frac{1}{2} m \omega_y^2 Y^2 \quad (\text{II.7a})$$

$$= H_x + H_y \quad (\text{II.7b})$$

In this case, the energy of each mode is conserved.

$$H_x = E_x$$

$$H_y = E_y$$

The one-dimensional harmonic oscillator Hamiltonians H_x , H_y may be taken as two independent isolating integrals. The trajectory would consequently be restricted to a two-dimensional surface in four-dimensional phase space.

Since we know that an n degree of freedom system possesses $2n-1$ independent integrals in general, we know that there must be three

integrals for this problem. The third integral may be taken to be the relative phase of the x and y oscillators ($\phi_x - \phi_y$), where ϕ_x is defined by

$$x = A_x \sin(\omega_x t + \phi_x)$$

and similarly for ϕ_y .

If the oscillator frequencies are incommensurable then the trajectory will never close on itself, and the motion will fill a two-dimensional surface, as mentioned above. In this case the phase difference is a non-isolating integral. However, if the oscillator frequencies are commensurable then the trajectory will be periodic, and the motion will not fill a two-dimensional surface, but will be confined to a line (a closed Lissajous figure). The phase difference will therefore be an isolating integral, and will specify the exact configuration of the Lissajous figure. (For example, if the frequencies ω_x and ω_y are equal, then the Lissajous figure will be an ellipse. If the two oscillators are out of phase of $\pi/2$ radians, then (if the amplitudes A_x, A_y are equal) the ellipse will be a circle; if the oscillators are in phase then the ellipse will degenerate into a straight line.)

The connection of these ideas with those previously discussed is that if the motion is quasiperiodic, then it is topologically equivalent to flow on an n-dimensional torus in 2n-dimensional phase space. The n-fold reduction in dimensionality of the region of phase space to which the trajectory has access implies that n independent isolating

integrals exist if the motion is quasiperiodic. These n isolating integrals may be taken to be the action variables.

The case treated in this section is separable, and is meant only to illustrate the concepts involved. For nonseparable cases, it is usually not possible to proceed analytically, although as will be shown later, progress can be made numerically.

A number of concepts can now be gathered together. If the nature of the n -degree of freedom problem is such that action and angle variables can be found, the motion will be quasiperiodic. This motion will be topologically equivalent to flow on an n -torus. The angle variables can be related to angles on the torus. Since the phase space is $2n$ -dimensional, and the motion is confined to an n -dimensional manifold, it follows that there are n independent action variables. Since the n independent isolating integrals determine the n -dimensional surface in phase space to which the trajectory is confined, we may say that the n action variables parameterize the n -torus. All separable systems have all of these properties. In Fig. II.3 is a visual aid which is intended to schematically illustrate that if one of the properties shown exists, then the others follow.

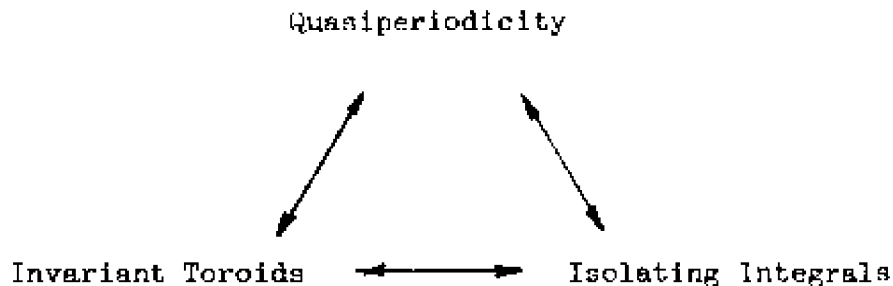


Fig. II.3

Visual Aid

2. Nonseparable Classical Systems

Now that the concepts of quasiperiodicity, invariant tori, and isolating integrals have been introduced, we are prepared to consider nonseparable systems. We will begin by discussing the work done by Hénon and Heiles¹⁴ (hereafter referred to as H & H).

H & H considered a system of two harmonic oscillators coupled by a nonlinear force. They wished to find out whether the system possessed a second isolating integral, independent of the energy. In order to detect the existence of this integral, they used a mathematical device known as a Poincaré surface of section.^{7,12} The usefulness of this technique stems from the fact that an isolating integral restricts the dimensionality of the region of phase space to which a trajectory has access.

In order to define a surface of section, let us consider a system in which the Hamiltonian is an integral of the motion (i.e. non-dissipative system). The motion in n -dimensional phase space will then be confined to the "energy shell" - an $(n-1)$ -dimensional volume in phase space. The Poincaré surface of section is a cross sectional display of this volume.

In order to more clearly illustrate the nature of a surface of section, let us consider a two degree of freedom system. For such a system, phase space is four-dimensional, and the motion is confined to a three-dimensional energy surface (or volume). Possible choices for a

surface of section are the x - p_x plane (with $y = 0$) or the y - p_y plane (with $x = 0$). For example, in order to display the intersection of the "energy shell" with the y - p_y plane (with $x = 0$), the trajectory is integrated until the x coordinate passes through zero. At that point, the values of p_y and y are recorded. The motion is then continued, recording p_y and y each time the trajectory pierces the $x = 0$ plane. (The trajectory could pass through $x = 0$ with either positive or negative p_x ; these crossings are recorded for only one choice, say $p_x > 0$. Notice also that values of p_y , y , and $x (= 0$ here) along with the condition $p_x > 0$ specify the position in phase space since p_x can be obtained from the energy equation.)

As an illustration, consider a two-dimensional harmonic oscillator.

$$H = \frac{p_x^2}{2m} + \frac{1}{2} m \omega_x^2 X^2 + \frac{p_y^2}{2m} + \frac{1}{2} m \omega_y^2 Y^2$$

If the y - p_y plane with $x = 0$ is taken for a surface of section, successive intersections of the trajectory will lie on an ellipse. Similarly, if the x - p_x plane with $y = 0$ is taken, the generated intersections will again lie on an ellipse. The two ellipses which are obtained will each contain independent information. In this case, the size of each ellipse will depend on the energy in the corresponding mode, or oscillator.

The use of a Poincaré surface of section in detecting the existence of an additional isolating integral independent of the energy

can be seen from the two-dimensional case. If no isolating integral independent of the energy exists, then the trajectory will have access to a three-dimensional region of phase space, and will therefore generate a sequence of intersections with the surface of section which will fill a two-dimensional region. However, if a second independent isolating integral exists, then by definition, the trajectory will have access to only a two-dimensional region of phase space. Since the intersection of this two-dimensional region with the surface of section will be a line, it follows that the trajectory will generate a sequence of intersections with the surface of section which form a curve. It is therefore possible to detect the presence of a second independent isolating integral simply by finding out whether successive points on the surface of section fill an area or line on a line. (It must be pointed out that if the Poincaré surface of section plot is generated using numerical methods, then the existence of a second isolating integral is only suggested to within numerical accuracy, not proven.)

The potential which H & H studied is given by

$$\mathcal{U}(x,y) = \frac{1}{2}(x^2 + y^2) + x^2y - \frac{1}{3}y^3 \quad (\text{II.8})$$

It is clear that for low energies (small amplitudes) the potential describes weakly coupled harmonic oscillators, while as the energy (or amplitude) increases, the cubic terms grow more rapidly than the quadratic terms, and the effect of the coupling increases.

A Poincaré surface of section which II & H observed for an energy $E = .08333$ is shown in Fig. II.4. Each set of points lying on a curve corresponds to a single trajectory. If the $x = 0$ plane is used for a surface of section, we have (since $p_x^2 \geq 0$)

$$\frac{1}{2} p_y^2 + \mathcal{U}(x=0, y) \leq E \quad (\text{II.9})$$

The outer contour in the diagram is given by the limit of this inequality.

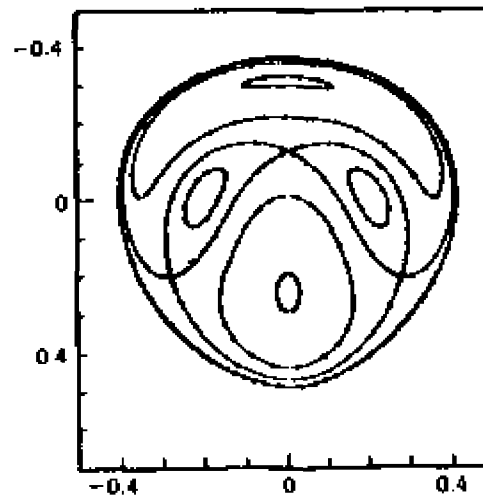
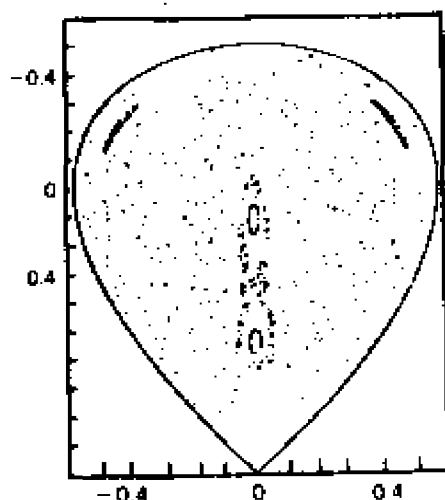


Fig. II.4

Surface of Section at Low Energy

In Fig. II.5 is shown a surface of section for $E = .16667$. All of the isolated points correspond to a single trajectory.



Surface of Section at High Energy

Fig. II.5

Clearly, the behavior of this trajectory differs from that shown in Fig. II.4. It is apparently more or less randomly filling an area instead of generating a curve.

Conclusions must be drawn carefully from the results published by H & H. The conclusions which they drew are that the motion at low energies is characterized by the existence of two independent isolating integrals, while the motion at high energies is characterized by the existence of only one isolating integral. In other words, they

concluded that motion at low energies, near the separable limit, is quasiperiodic, whereas motion at high energies is primarily "ergodic". (They used this term loosely, as will be discussed shortly. Let us refer to such trajectories as irregular.) H & H found that the transition from quasiperiodic behavior began at an energy of approximately $E = 0.11$, and that the fraction of quasiperiodic trajectories fell essentially linearly to approximately zero at the escape energy for the potential $E = 0.16667$.

Such computer experiments necessarily give an oversimplified view of the situation, however. The full complexity of non-separable dynamical systems is revealed by the theorems of Kolmogorov, Arnol'd and Moser (KAM),^{10,15,16} the study of area-preserving mappings,^{10c,d,17} and further numerical experiments, all of which have been reviewed by Ford.¹⁷

The KAM theorem establishes the preservation of quasiperiodic motion under small perturbations. KAM begin from unperturbed Hamiltonians that have only quasiperiodic trajectories, and they assume that the frequencies for these trajectories vary continuously as a function of the amplitudes. Hence as the amplitudes vary, the frequencies sweep through rational and irrational ratios; since the rational numbers form a set of measure zero among the reals, we may say that "most" of the unperturbed trajectories have irrational frequency ratios. Their theorem applies only to this subset of all the trajectories; about each unperturbed trajectory that has a rational frequency ratio (these trajectories

are dense) they delete a space that has a small but finite measure. They then can prove that the rest of the unperturbed trajectories - those with frequency ratios that are not rational and not sufficiently close to a rational - remain quasiperiodic under certain small perturbations. KAM have shown that these preserved tori dominate for small perturbations.

What happens to the trajectories with nearly rational frequency ratios depends upon the nature of the perturbation. There may exist non-separable systems that have only quasiperiodic trajectories, but if they do exist, they are the exceptional cases. Though little is known exactly, for the general non-separable Hamiltonian, it appears that those trajectories that are not covered by the KAM theorem tend to have so-called irregular behavior. The regions that can support irregular motion are dense, and of finite measure.

(With regard to referring to the irregular trajectories as ergodic, it must be pointed out that the existence of quasiperiodic trajectories of non-zero measure is inconsistent with ergodic behavior, as traditionally defined. This is because an ensemble average over phase space would include a set of positive measure of trajectories which remain forever on invariant tori. Ford¹⁷ suggests that for three or more degrees of freedom, cases may exist (commensurable zero-order frequencies) in which the volume of phase space occupied by quasiperiodic trajectories may be so small as to be physically insignificant, in which case he suggests that the motion may be ergodic "for all practical

purposes". The two degree of freedom case is unique in that irregular trajectories must remain trapped between invariant toroids. In that case a single ergodic trajectory cannot have access to even the entire irregular region, let alone to the quasiperiodic regions.)

These considerations permit a more complete interpretation of the H & K calculations. The limitations of computer accuracy make it appear that the low energy trajectories are entirely quasiperiodic, but in general we must expect the existence of irregular trajectories occupying very small but finite regions even arbitrarily close to $E = 0$. The quasiperiodic trajectories will dominate, however. Furthermore, an irregular trajectory may appear to be quasiperiodic within computer accuracy because it is trapped between two quasiperiodic trajectories. At high energies, however, the effects of the non-separable perturbation are larger, and irregular trajectories dominate.

B. The Nature of Quantum States

This thesis is primarily concerned with quantizing nonseparable multidimensional systems using semiclassical methods. Such methods use knowledge of the classical mechanical behavior of a system in order to obtain information about quantum mechanical behavior of the system. Until recently only one-dimensional systems, or separable multidimensional systems have been treated using semiclassical methods (Bohr-Sommerfeld quantization, WKB methods). Such systems always display quasiperiodic classical behavior, and semiclassical methods devised to

date have relied on this property. If nonseparable systems are to be treated semiclassically, then the extremely complicated classical behavior discussed in the previous section must be considered. Einstein¹⁸ appears to be one of the first to consider the quantization of nonseparable systems.

Einstein^{18,4d} pointed out that if the trajectory is plotted in configuration space (i.e. in the space defined by the coordinates q), and if one looks at an element $d\tau$, then each passage of the trajectory will give rise to a momentum vector p_k . Two possibilities arise: either the vectors p_k repeat, so that only a finite number belong to each $d\tau$, so that p_k can be written as a single- or many-valued function of q_k , or an infinite number of p_k pass through $d\tau$, so that p_k cannot be written as a function of q_k . The former case applies to a quasiperiodic trajectory such as the one shown in Fig. II.2a, and the latter case apparently applies to the "ergodic" trajectory shown in Fig. II.2b. Since all present semiclassical methods are based in one way or another on evaluating phase integrals, the question of whether the momentum can be expressed as a function of the coordinates is of the utmost importance.

Percival⁴ has speculated on the consequences of the transition from dominantly regular to dominantly irregular motion in classical mechanics. He postulates that there will exist some corresponding transition in quantum mechanics, and he refers to the quantum mechanical energy levels which are characterized by predominantly quasiperiodic motion in the classical limit as forming the regular spectrum; the levels characterized by predominantly "ergodic" motion in the classical limit he calls the irregular spectrum.

Percival compares the properties of the regular spectrum, and his postulated irregular spectrum. For the regular spectrum, he writes:^{4d}

R1. A quantal state may be labeled by the vector quantum number

$$n = (n_1, \dots, n_N)$$

R2. A state with quantum number n corresponds to those phase-space trajectories of the corresponding classical system that lie in an N -dimensional invariant toroid with action constants I_k given by quantum conditions

$$I_k = (n_k + \alpha_k/4)h$$

R3. The quantal state must resonate at frequencies close to those of the corresponding classical motion. Given two quantal states with one n_k differing by unity and the others the same, the Planck relation for their energy difference is

$$\Delta E_k = h\omega_k$$

where ω_k is a fundamental frequency on the corresponding toroid.

R4. A "neighboring state" to a state n^0 with energy E^0 is a state with vector quantum number n close to n^0 , with energy difference no more than a small multiple of the maximum

$$|\Delta E_n|.$$

R5. We now use the correspondence principle for weak perturbations, whose most well-known form is the correspondence principle for intensity of radiation. Under weak external

perturbations the state n^0 is much more strongly coupled to neighboring states than to other states, with the coupling tending to decrease rapidly with $|n - n^0|$.

For the irregular spectrum he postulates:

The correspondence principle predicts properties of an irregular spectrum in striking contrast to those of a regular spectrum:

11. There is no unambiguous assignment of a vector quantum number to a state Ψ_0 .

12. The discrete bound state quantal spectrum must tend to a continuous classical spectrum in the classical limit. The frequencies

$$[E(\bar{\Psi}) - E(\bar{\Psi}_0)]/h = \omega$$

for fixed stationary state Ψ_0 and varying Ψ form a discrete distribution that tends to the continuous distribution in ω . The distribution of levels of the irregular spectrum could take on the appearance of a random distribution.

13. By applying the correspondence principle for weak perturbations, there are no neighboring states in the sense of (R4) and (R5). Except for selection rules and accidents, a state of an irregular spectrum is coupled by a weak perturbation with intensities of similar magnitude to all those states of a similar energy that correspond to the same irregular

region of classical phase space. The number of such states is very large, of order

$$n_j^{N-1}$$

where n_j is a typical quantum number.

I4. The energies of the irregular spectrum are more sensitive to a slowly changing or fixed perturbation than those of the regular spectrum.

In order to test Percival's hypothesis about the irregular spectrum, Pomphrey^{4e} performed some numerical experiments on the system considered by Hénon and Heiles. Having added a parameter α to adjust the strength of the perturbation, he considered a Hamiltonian of the form

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(x^2 + y^2) + \alpha(x^2y - \frac{1}{3}y^3) \quad (\text{II.10})$$

He calculated energy levels quantum mechanically by choosing a basis set and diagonalizing a matrix. In order to determine the sensitivity of the energy levels to variations in the potential parameters, he varied α slightly, calculating a spectrum with α varying from 0.90 to 0.86 in steps of .001. The sensitivity to α was measured by considering second differences defined by

$$\Delta_i = \left| [E_i(\alpha + \Delta\alpha) - E_i(\alpha)] - [E_i(\alpha) - E_i(\alpha - \Delta\alpha)] \right| \quad (\text{II.11})$$

where i denotes the particular eigenvalue under investigation. Pomphrey found that of the seventy states investigated, twelve were substantially more sensitive to variations, and possessed second differences which were about an order of magnitude greater than those for the less sensitive states.

Though these results provide some evidence favorable to Percival's hypothesis, this evidence is not yet conclusive. Noid¹⁸ has repeated this calculation, but dividing the second differences by the energy; he could find no abrupt change that would suggest a qualitative change in the nature of the spectrum. In addition, he noted that some of the rather convoluted quasiperiodic trajectories that exist at high energies are very sensitive to perturbations, so any quantum states that are based on such trajectories must also be very sensitive.

In the next section, we will investigate current semiclassical methods. The classical mechanical nature of nonseparable systems, and the consequent effect on traditional quantization techniques and the quantum mechanical spectrum, as investigated by Einstein and Percival, should be kept in mind. Except for the method of Gutzwiller³, all present methods of semiclassical quantization are limited in their applicability to systems that have dominantly or entirely quasiperiodic classical behavior.

C. Semiclassical Methods for the Quasiperiodic Case

As discussed earlier, semiclassical methods use knowledge of the classical mechanical behavior of a system in order to obtain

information about the quantum mechanical state of the system. Semi-classical methods can be applied to both scattering and bound states, but we will only use it to calculate energy levels. As this section will show, the action variables introduced in the last section have a central role in semiclassical quantization methods. In order to illustrate this role, let us begin by reviewing the one-dimensional WKB method.

1. Review of One-Dimensional WKB method

Given the time independent Schrödinger equation

$$\frac{d^2\psi}{dx^2} + \frac{2m}{\hbar^2} [E - V(x)]\psi = 0 \quad (\text{II.12})$$

let us write the wavefunction ψ as

$$\psi = A e^{\frac{i}{\hbar}S}$$

(Since we will later need ψ for regions inaccessible to classical particles, S is not restricted to be real. Requiring S and $\ln A$ to be even functions of \hbar will ensure uniqueness of S and A .) If this form is substituted into the Schrödinger equation, the following exact equations for S and A are obtained:¹⁹

$$\left(\frac{dS}{dx}\right)^2 - 2m(E - V) = \hbar^2 \frac{d^2A}{dx^2} \quad (\text{II.13})$$

$$2 \frac{dA}{dx} \frac{dS}{dx} + A \frac{d^2S}{dx^2} = 0 \quad (\text{II.14})$$

The continuity equation (II.14) can be integrated to yield

$$A = \text{const} \cdot \left(\frac{\partial S}{\partial x} \right)^{-1/2} \quad (\text{II.15})$$

If the expression for A and its second derivative are now substituted into (II.13), the following equation for S is obtained

$$\left(\frac{dS}{dx} \right)^2 = 2m(E-V) + \hbar^2 \left[\frac{3}{4} \left(\frac{\frac{d^2 S}{dx^2}}{\frac{dS}{dx}} \right)^2 - \frac{1}{2} \left(\frac{\frac{d^3 S}{dx^3}}{\frac{dS}{dx}} \right) \right] \quad (\text{II.16})$$

So far, no approximations have been made, and eqns. II.15 and II.16 are rigorously equivalent to the Schrödinger equation. Let us now expand S in powers of \hbar^2 :

$$S = S_0 + \hbar^2 S_1 + \dots \quad (\text{II.17})$$

and substitute into (II.16). The WKB approximation consists of retaining only zero-order terms in \hbar ; the following equation results:

$$\left(\frac{dS}{dx} \right)^2 \approx \left(\frac{dS_0}{dx} \right)^2 = 2m [E - V(x)] \quad (\text{II.18})$$

Inspection of (II.16) shows that terms of higher order in \hbar may be neglected only where $E - V \neq 0$, and furthermore only where V does not vary so rapidly that higher derivatives of S become important. Equation (II.18)

is recognized as the time independent Hamilton-Jacobi equation (II.1) where $\alpha, = E$ and $W = S_0$. We see therefore that in the classical limit of $\hbar \rightarrow 0$ the quantum mechanics is approximated by classical mechanics.

The differential equation (II.18) may be integrated for two regions - that where $E > V(x)$, and that where $E < V(x)$. Let us use the definitions

$$k(x) \equiv \sqrt{\frac{2m[E - V(x)]}{\hbar^2}} \quad \text{for } E > V(x) \quad (\text{II.19})$$

and

$$\kappa(x) \equiv \sqrt{\frac{2m[V(x) - E]}{\hbar^2}} \quad \text{for } E < V(x) \quad (\text{II.20})$$

Using these abbreviations we see that the WKB solution to the Schrödinger equation is a linear combination of solutions

$$\psi(x) = \frac{\alpha}{\sqrt{k(x)}} \cos\left(\int_{x_1}^x k(x) dx + \phi\right) \quad \text{for } E > V(x) \quad (\text{II.21})$$

and

$$\psi(x) = \frac{1}{\sqrt{\kappa(x)}} \left[\gamma e^{\int_{x_1}^x \kappa(x) dx} + \delta e^{-\int_{x_1}^x \kappa(x) dx} \right] \quad \text{for } E < V(x) \quad (\text{II.22})$$

where $\alpha, \phi, \gamma, \delta$ are constants, and where x_1 is any constant for which the integral is convergent.

Notice that in the classically allowed region the wavefunction is oscillatory, but has a varying wavelength. In the classically forbidden region, the wavefunction is a combination of exponentially increasing or decreasing functions, but with varying growth or decay rates. If the potential were a constant, then the Schrödinger equation would have been exactly solvable, and would have yielded sines and cosines in the allowed regions, and increasing or decreasing exponentials in the forbidden regions. It is reasonable to expect that if the potential is allowed to vary slowly, the resulting wavefunction would be sines and cosines (or exponentials) but with slowly varying arguments. The condition for validity of the WKB approximation is therefore easily understood to be that the potential not vary significantly over the distance of one wavelength or decay length.

A difficulty arises in employing the WKB approximation when joining solutions defined in regions separated by a classical turning point (i.e. where $E - V = 0$). In the region of the turning point, the Hamilton-Jacobi equation does not approximate the Schrödinger equation, so the latter must be solved directly. As pointed out by Langer,²⁰ it is not necessary to solve the Schrödinger equation for the exact potential $V(x)$, but merely to approximate the potential by a linear function in the vicinity of the turning point. If this is done, the solution can be expressed directly in terms of Airy functions, or in terms of Bessel functions of order $1/3$. Airy functions have the property of being oscillatory in the classically allowed region, and exponential in the classically forbidden region. By employing the asymptotic representation

of the Airy function in the regions away from the turning point, the WKB solutions of the classically allowed region may be joined smoothly to the WKB solutions of the classically forbidden region.

If these steps are carried out, the following connection formulas result:¹⁹

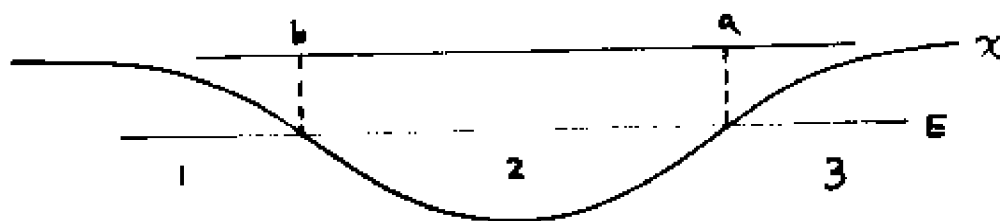
$$\left. \begin{aligned} \frac{1}{\sqrt{\kappa(x)}} \exp\left(-\int_x^b \kappa dx\right) &\longrightarrow \frac{2}{\sqrt{\kappa}} \cos\left(\int_b^x \kappa dx - \frac{\pi}{4}\right) \\ \frac{-1}{\sqrt{\kappa(x)}} \exp\left(\int_x^b \kappa dx\right) &\longleftarrow \frac{1}{\sqrt{\kappa}} \sin\left(\int_b^x \kappa dx - \frac{\pi}{4}\right) \end{aligned} \right\} \begin{array}{l} \text{barrier} \\ \text{on left} \end{array} \quad \begin{array}{l} \text{(II.23)} \\ \text{(II.24)} \end{array}$$

where b is the turning point with barrier to the left,

$$\left. \begin{aligned} \frac{2}{\sqrt{\kappa}} \cos\left(\int_x^a \kappa dx - \frac{\pi}{4}\right) &\longleftarrow \frac{1}{\sqrt{\kappa}} \exp\left(-\int_a^x \kappa dx\right) \\ \frac{1}{\sqrt{\kappa}} \sin\left(\int_x^a \kappa dx - \frac{\pi}{4}\right) &\longrightarrow \frac{-1}{\sqrt{\kappa}} \exp\left(\int_a^x \kappa dx\right) \end{aligned} \right\} \begin{array}{l} \text{barrier} \\ \text{on right} \end{array} \quad \begin{array}{l} \text{(II.25)} \\ \text{(II.26)} \end{array}$$

where a is the turning point with barrier to the right. These connection formulas may be safely used only in the direction of the arrows. If they are employed in the opposite direction, great care must be taken.

The WKB solution can be used in conjunction with the requirement of a single-valued wavefunction in order to quantize the energy levels for a one-dimensional potential well.



One-Dimensional Single Well

Fig. II.6

Region 2 is the classically allowed region; regions 1 and 3 are classically forbidden. a and b are the classical turning points.

Boundary conditions require that the wavefunction in region 1 decrease exponentially as $x \rightarrow -\infty$.

$$\psi_1(x) = \frac{1}{\sqrt{\kappa(x)}} \exp\left(-\int_x^b \kappa(x) dx\right) \quad (\text{II.27})$$

The connection formula (II.23) can be used to connect the wavefunction in this region to the wavefunction in region 2. ψ_2 will then be expressed in terms of an integral taken with reference to the left turning point.

$$\psi_2(x) = \frac{2}{\sqrt{k}} \cos\left(\int_b^x k(x) dx - \frac{\pi}{4}\right) \quad (\text{II.28})$$

Using the fact that

$$\int_b^x k dx = \int_b^a k dx - \int_x^a k dx \quad (\text{II.29})$$

Ψ_2 can be reexpressed in terms of an integral taken with reference to the right hand turning point:

$$\begin{aligned} \Psi_2(x) = & -\frac{2}{\sqrt{k(x)}} \cos\left(\int_b^a k dx\right) \sin\left(\int_x^a k dx - \frac{\pi}{4}\right) \\ & + \frac{2}{\sqrt{k(x)}} \sin\left(\int_b^a k dx\right) \cos\left(\int_x^a k dx - \frac{\pi}{4}\right) \end{aligned} \quad (\text{II.30})$$

Now boundary conditions also require that Ψ_3 be a decreasing exponential:

$$\Psi_3(x) = \frac{1}{\sqrt{k(x)}} e^{-\int_a^x k(x) dx} \quad (\text{II.31})$$

If the connection formula (II.25) is used, an alternative expression for Ψ_2 is obtained

$$\Psi_2 = \frac{2}{\sqrt{k(x)}} \cos\left(\int_x^a k dx - \frac{\pi}{4}\right) \quad (\text{II.32})$$

Single valuedness of the wavefunction requires that the two expressions for Ψ_2 be the same. This will occur only if the following condition is satisfied:

$$\int_b^a k(x) dx = (n + \frac{1}{2}) \pi \quad (\text{II.33})$$

This is the semiclassical quantization condition. Noting that the momentum $p = \hbar k$, and requiring k (or p) to be positive as x is increasing, and

negative as x is decreasing, the quantization condition can be written as

$$J = \oint p dx = (n + 1/2) h \quad (II.34)$$

We now see the special role of the action variable, which was mentioned earlier. The phase integral is taken over one cycle of classical motion, between libration limits (turning points) as required in the definition (II.3).

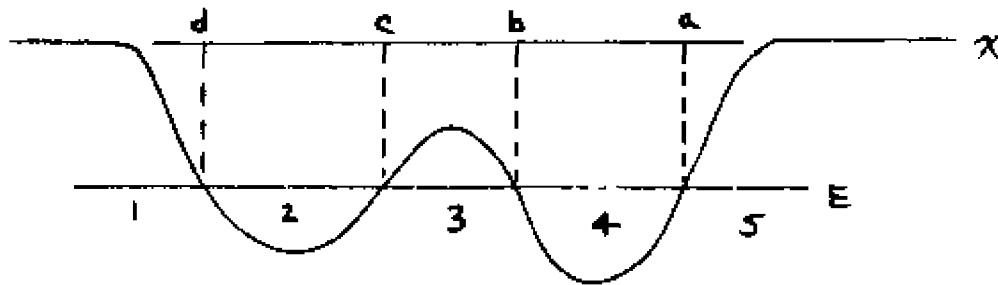
The fact that half integral quantization is obtained is directly related to the presence of the $\pi/4$ term in the connection formulas. This $\pi/4$ phase shift entered in the asymptotic form for the Airy function. It is customary to interpret this as the phase shift which appears after the trajectory has passed through the caustic.

It is often incorrectly assumed that the correct quantization within the semiclassical scheme is always given by

$$J = \left(n + \frac{m}{4} \right) h \quad (II.35)$$

where m is the number of turning points encountered in a cycle of the motion ($m = 2$ here). The correct quantization is obtained from the quantum mechanical boundary conditions. The above expression is obtained if the wavefunction is exponentially decreasing on both sides of the allowed region. However, if the wavefunction is not purely a decreasing function in the forbidden region, a modified quantum condition is obtained. Appendix II treats the case of a one-dimensional symmetric

double well as an example. The potential for this case is shown in Fig. II.7.



One-Dimensional Double Well

Fig. II.7

Although region 3 is classically forbidden, the wavefunction there may contain both increasing and decreasing exponential terms. As shown in Appendix II, if the WKB connection formulas are applied (they must be applied in the wrong direction at one point) the following transcendental quantization condition results

$$\tan\left(\int_{\substack{b \rightarrow a \\ \text{or} \\ d \rightarrow c}} k dx\right) = \pm 2 \exp\left(\int_c^b \kappa dx\right) \quad (\text{II.36})$$

where the + sign leads to a symmetric state, and the - sign leads to an antisymmetric state. Notice that the integral inside the exponential is over the forbidden region 3. If it is assumed that the barrier between the two wells is wide, the quantization condition may be expanded to yield

$$\int_b^a k dx \simeq (n + 1/2) \pi \mp \frac{1}{2} \exp\left(-\int_c^b k dx\right) \quad (\text{II.37})$$

Comparison with equation (II.33) shows that the double well problem requires a correction to the usual half-integral quantization. This calculation also shows that the splitting between the two previously degenerate single-well states can be found without going outside the WKB formalism.

2. Multidimensional Semiclassical Quantization

This thesis is primarily concerned with quantizing multidimensional nonseparable problems. As a step toward this end, let us consider a system of two uncoupled harmonic oscillators. Let the Hamiltonian be given by

$$H = \frac{1}{2} (p_x^2 + \omega_x^2 x^2) + \frac{1}{2} (p_y^2 + \omega_y^2 y^2) \quad (\text{II.38})$$

If we plot the motion of this system in x-y space, the trajectory will form a Lissajous figure similar to that of Fig. II.2a. However, in this case the motion will be confined to a rectangular region. The four corners of the rectangle touch an ellipse which represents the limit of the energetically allowed region. Since two independent isolating integrals exist (for example, the energy of each oscillator), the motion does not fill the energetically accessible region. The lines which

bound the motion are called caustics. The organized nature of the manifold to which the trajectory belongs is evident. In this case, the manifold will have four sheets everywhere, which are joined along the caustics.

For this separable problem, we can treat the two degrees of freedom separately. Let us write the Hamiltonian for one degree of freedom as

$$H_i = \frac{1}{2} (p_i^2 + \omega_i^2 x_i^2) \quad (II.39)$$

The potential is a parabola, and we are solving for the motion of the particle in a well. Solving the classical problem in terms of action-angle variables, we find that the energy is given as

$$E_i = J_i \frac{\omega_i}{2\pi} \quad (II.40)$$

where

$$J_i = \oint_{c_i} p_i dx_i \quad (II.41)$$

The integral is taken over a path c_i between libration limits (turning points). Since the motion is that of a particle in a single well, half-integral quantization follows, as in equation (II.34).

$$J_i = (n_i + \frac{1}{2}) h \quad (II.42)$$

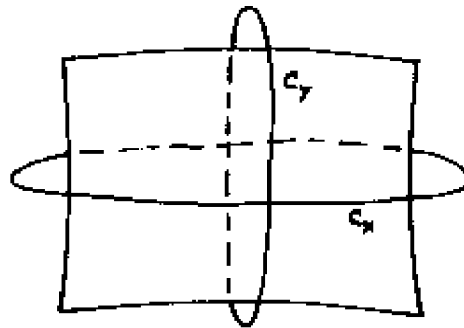
Therefore

$$E_i = (n_i + \frac{1}{2}) \hbar \omega_i \quad (II.43)$$

The total energy of a quantum state is therefore given by

$$E_{tot} = (n_x + \frac{1}{2}) \hbar \omega_x + (n_y + \frac{1}{2}) \hbar \omega_y \quad (II.44)$$

There are several points to notice for this case. First of all, two independent phase integrals must be quantized for this two degree of freedom problem. Secondly, by plotting the integration paths of equation (II.41) on the trajectory diagram shown in Fig. II.8,



Integration Paths in Configuration Space

Fig. II.8

we can see that the integrations for the individual one-dimensional problems correspond to calculating path integrals over two topologically independent paths in the two-dimensional problem. (If mapped onto the

invariant torus the paths would be topologically independent. By this we mean that one path cannot be topologically deformed into the other on the toroidal surface. See Fig. II.9. This topological independence manifests itself in configuration space in that topologically independent paths will touch a different pair of caustics.) Since this problem was separable, we paid no attention to the y motion when we were calculating the x phase integral, and vice versa. Therefore, we see that the integration paths do not lie on the actual trajectory, but are merely arbitrary paths connecting opposite caustics. (As in the case treated in Appendix I, the integral is path independent because the argument of the integral is an exact differential; in particular because the generating function is separable.)

The final point to notice is that the path integrals each touched exactly two caustics and were quantized using half-integral quantization. As we will discuss, the proper quantization for a given integration path depends on how many caustics that path touched.

We would finally like to consider semiclassical quantization methods for nonseparable multidimensional cases. These methods in effect overlook any irregular orbits present, and seek to quantize the quasiperiodic motion. A nonseparable system with n degrees of freedom requires n quantization conditions, just as a separable n degree of freedom problem would. Since the classical motion is treated as quasiperiodic, we assume the existence of n independent isolating integrals, which we will choose to be the action variables. Because of the

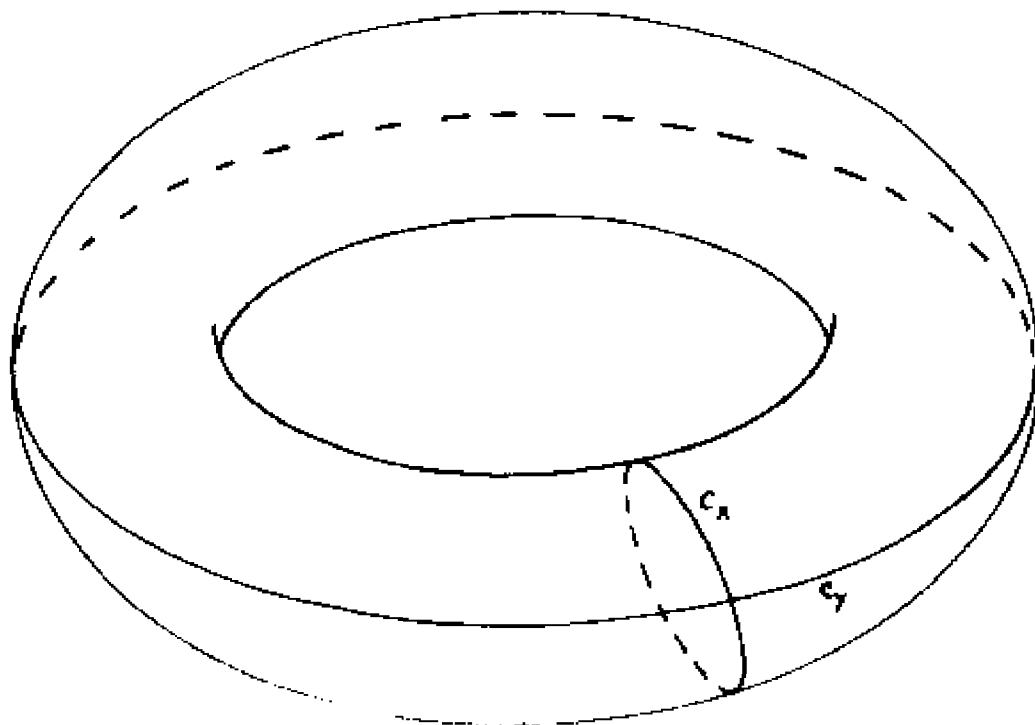


Fig. II.9. Integration Paths in Phase Space.

nonseparability, however, we must modify our definition of the action variable. Recall our earlier definition:

$$J_i = \oint p_i dq_i \quad (\text{II.3})$$

where the integral is taken over one cycle of q_i . There are two problems here. First of all, the motion which we will consider does not lead to straight line caustics enclosing rectangular regions. The caustics may be distorted, so much so in fact, that a straight line may not pass through opposite caustics without having to leave the allowed manifold. Quantization will still require phase integrals to be evaluated along n topologically independent paths, but it might not be possible to choose straight line paths.

Secondly, and more importantly, the action variable defined in (II.3) is no longer path independent. This is because the generating function W is not separable (by assumption). The resolution of this problem is found by noting that

$$\sum_{i=1}^n p_i dx_i \quad (\text{II.45})$$

is an exact differential and will therefore lead to a path independent integral. Therefore let us define the action variable as

$$J_k = \oint_{C_k} \vec{p} \cdot d\vec{x} \quad (\text{II.46})$$

where n independent action variables are defined by integrals taken over n topologically independent paths.^{18,1} (As before this will ensure that we are integrating around the invariant torus in n independent ways.) This definition reduces to the previous one in the separable case provided that the integration paths are chosen such that q_1 passes through one cycle, while the other coordinates are either held constant, or at least prevented from passing through a full cycle.

The only point which remains to be settled for the non-separable case is the quantization of the action. Should the quantization be half-integral, integral, or possibly something else? The answer is that it depends on the paths c_k chosen for the phase integrals.

Recall that for the separable case the quantization was half integral if the phase integral was done over one cycle between libration limits

$$J = (n + \frac{1}{2}) h \quad (II.34)$$

If for example, the path were chosen to cover two cycles instead of one, the result from the phase integral would be doubled

$$\begin{aligned} J_{2 \text{ cycles}} &= (2n + 1) h \\ &= m h \end{aligned} \quad (II.47)$$

where $m = 2n + 1$ equals an odd integer. If the path chosen were such that both the x motion and the y motion passed through a full cycle,

the resultant phase integral would be the sum of the phase integrals for separate x and y cycles

$$\begin{aligned} J_{\text{sum}} &= (n_x + \frac{1}{2}) h + (n_y + \frac{1}{2}) h \\ &= m' h \end{aligned} \tag{II.48}$$

where $m' = n_x + n_y + 1$ equals an integer. Until now, we have considered only simple paths in order to quantize. However, it is clear that more complicated paths, chosen as combinations of simple paths, can be quantized as long as n topologically independent paths are chosen.

Keller²¹ has written down quantization conditions for non-separable problems. The key to obtaining the correct quantization is to count how many times the integration path came in contact with a caustic. Keller's quantum condition is:

$$J \equiv \oint \sum_i p_i dq_i = \left[n + \frac{m}{4} \right] h \tag{II.49}$$

where m is the total number of times the integration path touches a caustic. (Keller's quantization condition is actually more general than this. It also allows for the possibility of the integration path passing through a focus, or through the intersection of two or more caustics.)

Keller's result is obtained by requiring the wave-function to be single valued, and by including a $\pi/2$ phase delay each time the

integration path touches a caustic. Appendix III contains a discussion of the method of constructing a semiclassical wavefunction for a non-separable system. The source of the $\pi/2$ phase delay at a caustic is shown.

(Just as we found for the one-dimensional case that half-integral quantization was correct only for single well problems, Keller's quantization is correct only for multidimensional generalizations of the single well problem. If the classical system should possess dynamical or other barriers which result in two or more wells, then the correct procedure within the WKB formalism requires that phase integrals over the classically forbidden region be calculated, as in Appendix II. As yet, no one has tried to include such effects in cases treated.)

By quantizing the action variables defined in equation (II.46), using Keller's quantization condition, multidimensional nonseparable systems may in principle be quantized. In the next section we review the methods which have been used to date in order to carry out the quantization.

3. Calculational Methods

Most methods for semiclassical quantization of non-separable multidimensional systems have used one of two main approaches. The first approach is to quantize phase integrals calculated in the original coordinates. The second approach is to seek a canonical transformation from the action-angle variables of an unperturbed separable case to the

proper action-angle variables of the perturbed case. Methods which use either of these approaches are of necessity limited to treating quasi-periodic motion, since only then does the invariant torus exist on which phase integrals can be defined and action variables calculated.

a. Numerical Trajectory Calculations

Several papers on semiclassical quantization have been published by Marcus and co-workers. The first which I will discuss was written by Eastes and Marcus.^{1a} The Hamiltonian which they considered is given by

$$H = \frac{1}{2} (p_x^2 + p_y^2 + \omega_x^2 x^2 + \omega_y^2 y^2) + \lambda x (y^2 + \eta x^2) \quad (\text{II.50})$$

and the procedure which they used is as follows. Parameters ω_x , ω_y , λ , η for the Hamiltonian were chosen. This specified the exact system to be quantized. The classical trajectory was then generated numerically by integrating Hamilton's equations of motion using a predictor-corrector method. After a sufficient number of steps, the trajectory when plotted formed a slightly distorted Lissajous figure, similar to that shown in Fig. II.2a.

The phase integrals were then calculated numerically from the trajectory information. The two topologically independent paths along which the phase integrals were evaluated were chosen for convenience to be along caustics. The path integrals were calculated using as the value

for the momentum in the integral the value provided from the trajectory by the tangential component of the momentum at that point. An interpolation scheme was used to search for initial conditions which led to correctly quantized phase integrals. Convergence was rapid; a total of four to five trajectories had to be generated and quantized for each energy level in order to provide five significant digits accuracy in the energy. The agreement with quantum mechanical methods was excellent.

Since the method involved integrating along a caustic, it was possible to treat only systems which produced fairly simple caustics. For this reason, Hamiltonians with frequencies related by the ratio of small integers could not be treated (such systems can lead to very complicated caustics). Furthermore, as the effect of the perturbation increased for higher energies, the shape of the region bounded by caustics changed from a slightly distorted box to a greatly distorted box ultimately bounded by folded caustics, making it inconvenient to apply the method.

A modified version of this theory, which overcame some of the difficulties associated with integrating along caustics, was presented in a paper by Noid and Marcus.^{1b} In this method, the trajectory was generated numerically as before, but the integration paths for the phase integrals were not chosen to be along the caustics, but along the lines $x = 0$, and $y = 0$. In practice, their method was to quantize action variables calculated by integrating around two topologically independent invariant curves of separate Poincaré surfaces of section.

The phase integrals were quantized using the same iterative scheme as the previous method used. Again, a total of four to five trajectories had to be generated and quantized for each level in order to provide five significant digit accuracy in the energy.

The method of Noid and Marcus is able to treat more cases than that of Eastes and Marcus; however the restriction to integrating along the straight lines $x = 0$ and $y = 0$ still prevents the method from treating some cases. As mentioned earlier, if the frequencies in the unperturbed part of the Hamiltonian (II.50) are related by the ratio of small integers (low order commensurability of the unperturbed frequencies) the resultant caustics may be very complicated. For example, if $\omega_x = \omega_y = 1$, trajectories like those figures II.10 and II.11 can result.

In order to treat such cases, Noid and Marcus eliminated the restriction of generating the Poincaré surface of section from intersections of the trajectory with a straight line integration path.^{1c} Instead the topologically independent integration paths were allowed to be curved, giving a curvilinear Poincaré surface of section.

The detailed considerations for the commensurable case are as follows. The Hamiltonian chosen is given by

$$H = \frac{1}{2} (p_x^2 + p_y^2 + x^2 + y^2) + \lambda x (y^2 - \frac{1}{3} x^3) \quad (\text{II.51})$$

where λ is the anharmonic coupling constant. This is the Hamiltonian which Hénon and Heiles used, aside from the parameter λ . Expressed

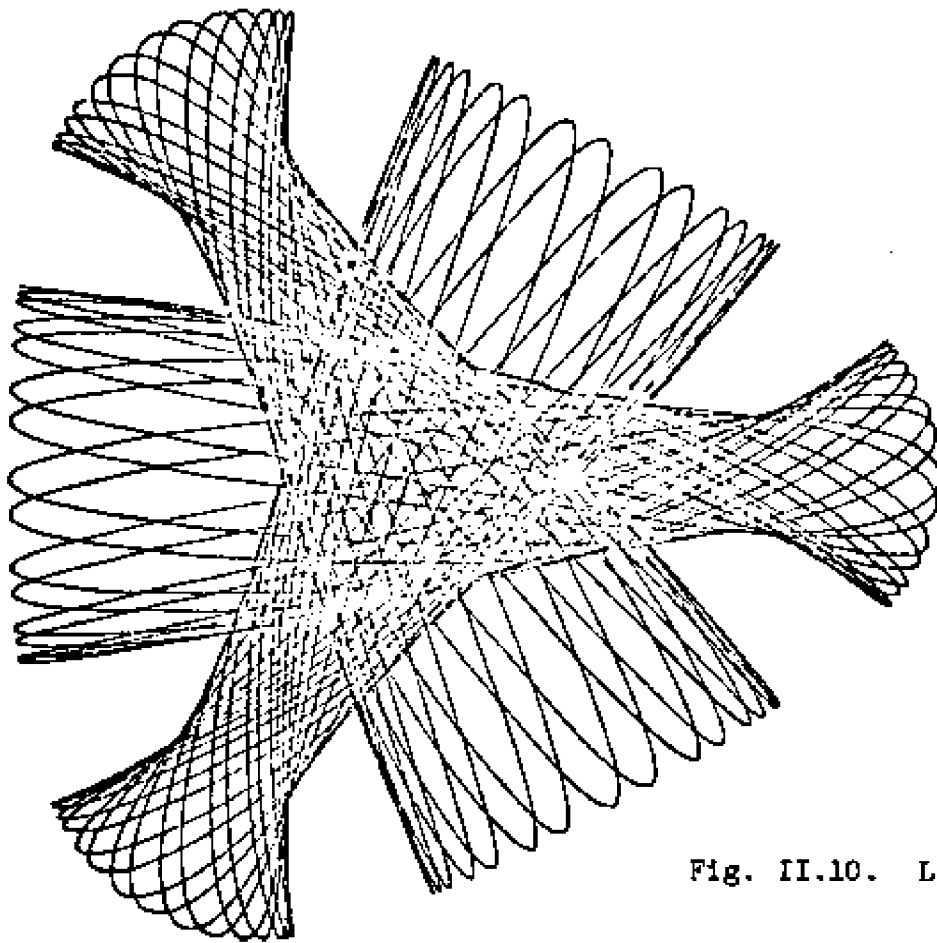


Fig. II.10. Libration Trajectory

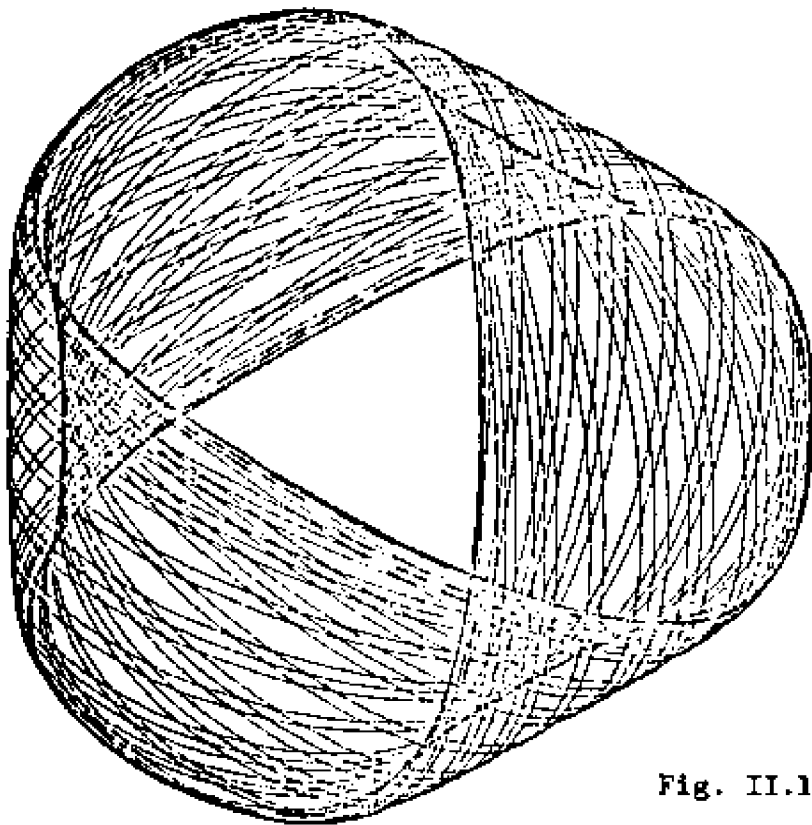


Fig. II.11. Rotation Trajectory

in polar coordinates (with $x = r \cos \theta$, $y = r \sin \theta$), the Hamiltonian becomes

$$H = \frac{1}{2} \left(p_r^2 + r^2 + \frac{p_\theta^2}{r^2} \right) - \frac{1}{3} \lambda r^3 \cos 3\theta \quad (\text{II.52})$$

Examples of trajectories generated by integrating Hamilton's equations using this Hamiltonian are those shown in Fig. II.10 and II.11. Figure II.10 has a low angular momentum, and Fig. II.11, a high angular momentum. As can be seen, two classes of trajectories have emerged. Noid and Marcus referred to the motion in Fig. II.10 as a libration, and that of Fig. II.11 a rotation.

If the internal angular momentum is nonzero, the trajectory for the unperturbed Hamiltonian is an ellipse. A manifold is created by rotating the ellipse around the origin. This corresponds to selecting the same energy and angular momentum, but selecting a different starting direction for the orbit. The inner and outer concentric circles which bound the manifold are caustics. The phase integrals are calculated by integrating over the manifold along two topologically independent paths and quantizing using Keller's quantum condition. Two possible paths are shown in Fig. II.12. Path A, a circle concentric with the center, touches no caustics, so the correct quantization for the phase integral is

$$\oint p_\theta d\theta = 2\pi \ell \quad (\hbar = 1) \quad (\text{II.13})$$

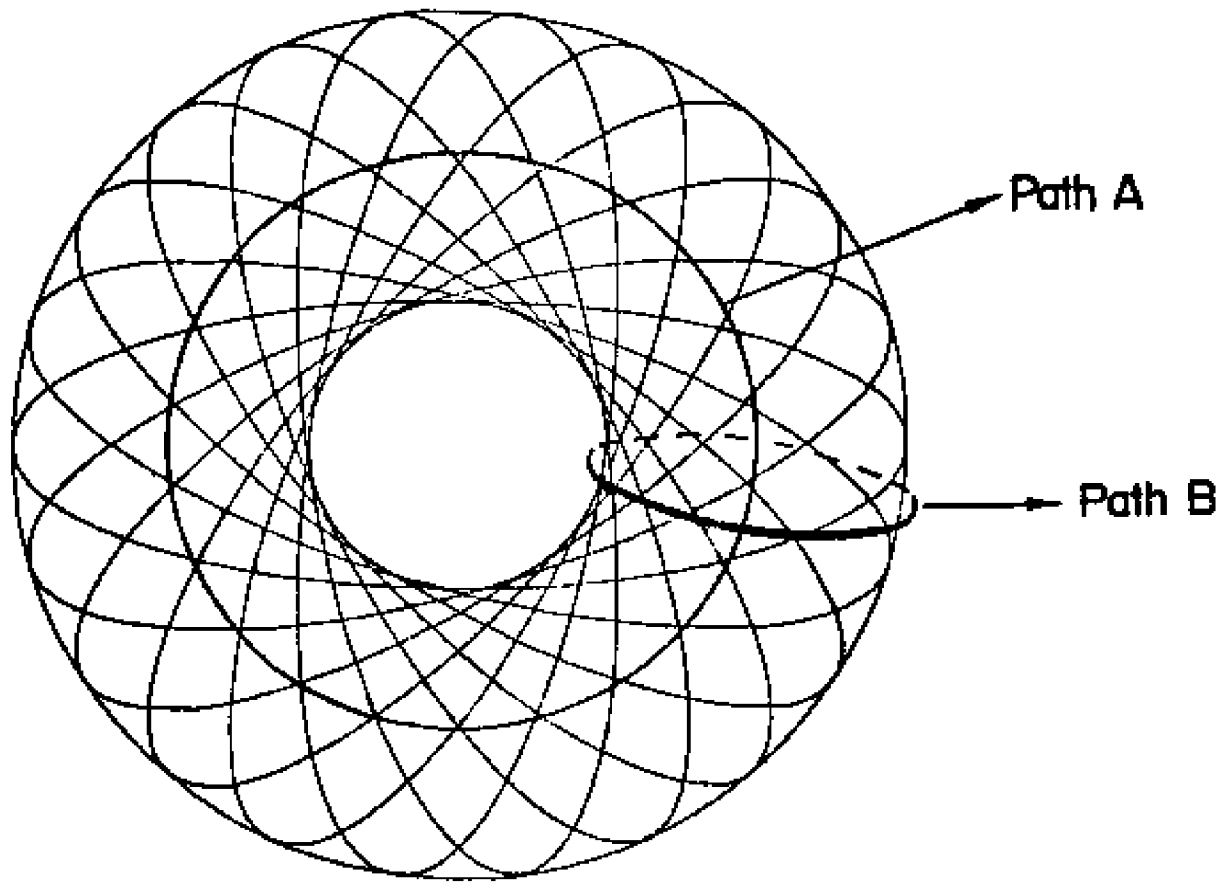


Fig. II.12. Trajectories for the Unperturbed System.

where l is an integer. Path B touches two caustics, so the correct quantization is

$$\oint p_r dr = 2\pi (n_r + \frac{1}{2}) \quad (\text{II.54})$$

where n_r is an integer. An alternative integration path would be along one of the ellipse trajectories. Such a path would touch the outer and inner caustics each twice. Therefore the correct quantization would be

$$\oint_{\text{traj}} p_x dx + p_y dy = 2\pi (n + \frac{1}{2}) \quad (\text{II.55})$$

where n is an integer. This integration path can be written in terms of the previous two as the sum of two r -cycle phase integrals and a θ -cycle phase integral.

$$\oint_{\text{traj}} p_x dx + p_y dy = 2 \oint p_r dr + \oint p_\theta d\theta$$

Therefore

$$n = 2n_r + l$$

relates the quantum numbers. Of course, there are only two independent quantum numbers.

Using integration paths similar to Path A and Path B of Fig. II.12, Noid and Marcus quantized the Poincaré surfaces of section for perturbed rotation cases. The numerical procedure was the same as discussed for their previous paper - namely generate a trajectory, use

crossings to generate two independent Poincaré surfaces of section, and iterate to quantize.

The libration cases were a bit more complicated to treat. I will review the procedure which Noid and Marcus used in detail since we will later make comparisons to this case.

As mentioned earlier, the libration cases occurred for low internal angular momentum. As inspection of the Hamiltonian II.52 shows, the anharmonic part of the potential causes three troughs to exist in the potential. If the orbital energy is low enough, the trajectory will be trapped on one of these troughs. This behavior is very similar to that of the one-dimensional double well treated in Appendix II. The correct quantization procedure within the WKB formalism would be a two dimensional generalization in which phase integrals were calculated over the classical forbidden region. In particular, simple half-integral quantization of the trajectory trapped in one trough would not be correct.

Noid and Marcus chose to ignore effects from tunneling between the troughs, and to simply evaluate a phase integral along an A-type path (Fig. II.12), including contributions only from the classically allowed regions. In effect this assumes that tunneling is so strong that no phase shift occurs in passage through the forbidden region.

The contributions from the three troughs are identical, so only one was calculated. The phase integral along path A over one trough is topologically equivalent to a phase integral over a path $x = 0$ for that trough. Therefore the quantization formula is:

$$\int_{\text{one trough}} p_{\theta} d\theta = \oint_{x=0} p_r dy = \frac{1}{3} 2\pi\ell \quad (\text{II.56})$$

Observe that for $\ell = 0$, we have $\oint p_{\theta} d\theta = 0$. This is actually the condition least likely to lead to strong tunneling because such motion must be confined to the narrowest possible region in the trough (so that the phase integral will go to zero). However, they say that the energy is very insensitive to ℓ ; hopefully this makes the neglect of correct tunneling effects less critical.

The other topologically independent phase integral was calculated by integrating along one cycle of the trajectory (an "open" ellipse), and joining the ends along a $y = 0$ invariant curve.

The results found by Noid and Marcus with $\lambda = \sqrt{.0125}$ for both librations and rotations are shown in Table IV.2 (along with results from our method, to be discussed in Chapter IV).

The percentage of disagreement (for rotations, as well as librations) with the quantum mechanical calculations is much larger for this commensurable case than for the incommensurable cases treated in their earlier papers. This should not be taken as an indication of unsuitability of quantizing curvilinear Poincaré surfaces of section, but merely as an indication that the semiclassical approximation is less accurate for this case.

In summary, the method of Eastes, Noid and Marcus is to quantize topologically independent phase integrals using numerical

methods. The practical application of the method may be complicated by the difficulty of choosing an integration path which avoids folds in the caustics. The fact that the integration path is plotted is an advantage since the proper quantization can be determined by counting how many times the integration path touches a caustic. (Later related work by Marcus, et al. appears in Id.e.)

b. Methods for Transformation to Angle-Action Variables

The next methods to be discussed take a very different approach to quantization. Instead of numerically evaluating phase integrals, these methods seek to transform directly to the proper angle-action variables for the perturbed system.

Two methods will be discussed in this section. The first is a method by Born²². The second is a method by Chapman, Garrett and Miller,^{1a} which is closely related to Born's method.

The essential procedure consists of three main steps. The first is to choose a separable Hamiltonian which can be considered an unperturbed limit of the complete Hamiltonian. The second step is to solve the Hamilton-Jacobi equation for the unperturbed Hamiltonian in order to obtain angle-action variables for the unperturbed problem. The third step is to seek a canonical transformation from angle-action variables of the unperturbed problem to the proper angle-action variables for the complete Hamiltonian. It is in the means of carrying out the third step that the two methods differ. I will outline both methods here.

Born's procedure begins by expanding the Hamiltonian in a power series in a small parameter λ :

$$H = H_0 + \lambda H_1 + \lambda^2 H_2 + \dots \quad (\text{II.57})$$

Angle-action variables (w^0, J^0) are obtained for the unperturbed Hamiltonian H_0 .

The generating function S for transformation to new angle-action variables (w, J) is expanded in λ :

$$S = S_0 + \lambda S_1 + \lambda^2 S_2 + \dots \quad (\text{II.58})$$

Finally the new Hamiltonian $K(J)$ is expanded in λ :

$$K = K_0 + \lambda K_1 + \lambda^2 K_2 + \dots \quad (\text{II.59})$$

These power series are now substituted into the Hamilton-Jacobi equation

$$H(w^0, J^0) = K(J) \quad (\text{II.60})$$

and the result is separated by powers of λ into an infinite set of equations which are equivalent to the original H-J equation (II.60).

The first equation is simply the zero-order approximation

$$H_0(J) = K_0(J) \quad (\text{II.61})$$

All higher orders n are of the form

$$\sum_k \frac{\partial H_0}{\partial J_k} \frac{\partial S_n}{\partial w_k^0} = K_n(J) - \bar{\Phi}_n \quad (\text{II.62})$$

where $\bar{\Phi}_n$ is a function of w^0 and J .

The set of equations is solved successively. The procedure involves expanding the Hamiltonian terms H_n in a Fourier series with known coefficients, and expanding the generating function S_n in a Fourier series with coefficients to be determined. The Fourier expansions are substituted into the equation to be solved, and the unknown Fourier coefficients for S_n are found by comparing terms. The function $\bar{\Phi}_n$ depends only on results from previous stages.

While Born's procedure consists in solving a perturbation expansion order by order, Miller's method attempts to carry out the transformation to infinite order directly by seeking to solve the problem exactly by numerical methods. Miller writes the original Hamiltonian as

$$H(x, p) = \frac{p^2}{2\mu} + V_0(x) + V(x) \quad (\text{II.63})$$

where $(x, p) = (x_i, p_i)$ $i = 1, f$ are Cartesian coordinates and momenta, and f is the number of degrees of freedom. The unperturbed potential $V_0(x)$ is separable. Miller then transforms to angle-action variables (q, n) for the unperturbed motion. For the harmonic case,

$$H_0(n) = \omega \cdot (n + \frac{1}{2}) \equiv \sum_i \omega_i (n_i + \frac{1}{2}) \quad (\text{II.64})$$

He then writes the H-J equation for transforming from (q, n) to angle-action variables of the complete Hamiltonian:

$$E(N) = H_0 \left(\frac{\partial F(q, N)}{\partial q} \right) + V \left(q, \frac{\partial F(q, N)}{\partial q} \right) \quad (\text{II.65})$$

where F is a type-2 generating function and the Hamiltonian $E(N)$ is the energy. Miller then notes that the zero-order transformation would be an identity transformation, and therefore chooses to write the generating function F in terms of an identity generator plus a generating function G

$$F(q, N) = q \cdot N + G(q, N) \quad (\text{II.66})$$

With this change, the H-J equation becomes with H_0 taken to be a harmonic oscillator Hamiltonian:

$$E(N) = \omega \cdot (n + \frac{1}{2}) + \omega \cdot \left(\frac{\partial G(q, N)}{\partial q} + V \left(q, N + \frac{\partial G(q, N)}{\partial q} \right) \right) \quad (\text{II.67})$$

Miller requires that G be a periodic function of q . This follows by assuming that the wavefunction can be expressed in the WKB approximation

$$\Psi_N(q) = \langle q | N \rangle \sim \exp \left[\frac{i}{\hbar} F(q, N) \right] \quad (\text{II.68})$$

and requiring that the wavefunction be single-valued. Therefore G can be written as

$$G(q, N) = i \sum_k' B_k e^{ik \cdot q} \quad (\text{II.69})$$

where the prime indicates that the constant term is omitted from the sum.

With the next step, Miller departs from Born's method. The Fourier expansion for G is substituted into the H-J equation (II.67), and then the equation is multiplied by $e^{-ik \cdot q}$, and integrated over q . This results is an integral equation equivalent to the H-J equation.

$$E(N) \delta_{k,0} = \omega \cdot (N + \frac{1}{2}) \delta_{k,0} - (\omega \cdot k) B_k + (2\pi)^{-f} \int_0^{2\pi} dq e^{-ik \cdot q} V(q, N - \sum_{k'} k' e^{ik' \cdot q} B_{k'}) \quad (\text{II.70})$$

For $k \neq 0$, this equation yields a set of coupled integral equations for the unknown Fourier coefficients B_k :

$$B_k = \frac{(2\pi)^{-f}}{\omega \cdot k} \int_0^{2\pi} dq e^{-ik \cdot q} V(q, N - \sum_{k'} k' e^{ik' \cdot q} B_{k'}) \quad (\text{II.71})$$

For $k = 0$, the energy is given in terms of the B_k :

$$E(N) = \omega \cdot (N + \frac{1}{2}) + (2\pi)^{-f} \int_0^{2\pi} dq V(q, N - \sum_{k'} k' e^{-ik' \cdot q} B_{k'}) \quad (\text{II.72})$$

Miller solves (II.71) for the Fourier coefficients using a numerical recursive iteration which involves evaluating the Fourier integral on a grid of points. He states that after one iteration his result agrees with Born's first order result, but that after that the methods are not equivalent.

In summary, the method of Chapman, Garrett and Miller, is to transform directly to the proper angle-action variables for the complete Hamiltonian by numerically solving a set of coupled integral equations which are equivalent to the Hamilton-Jacobi equation. (An application of the method of Miller, et al. appears in 2c.)

It should be pointed out that the methods of Born and of Miller, et al. are bound to be divergent. The source of the divergence is due at least in part to the famous problem from astronomical perturbation theory known as the small divisor difficulty.^{10c} A manifestation of the problem, for the case of a harmonic unperturbed Hamiltonian can be seen by inspecting eqn. (II.71). The denominator contains the factor

$\sum_{\mathbf{l}} w_{\mathbf{l}} k_{\mathbf{l}} = w \cdot k$. If the frequencies of the unperturbed motion are related by the ratio of integers (commensurability condition) then the denominator for some terms will vanish. Worse yet, even if the unperturbed frequency-ratios are irrational, since these numbers can be approximated to an arbitrary degree by rational numbers, a sufficient number of denominators will come arbitrarily close to zero to ensure the divergence of the sum. Born's method also suffers from the small divisor difficulty.

Another aspect of the divergence of both Born's and Miller's method is that they are bound to fail for multidimensional systems which possess a dense set of "ergodic" orbits embedded among the quasi-periodic orbits. The reason is that the convergence of these methods would imply that the motion actually was purely quasiperiodic. For such cases these methods would therefore be predicting behavior which violated

the true behavior of the system. Therefore the methods must be divergent in general.

The fact that the methods described here will diverge does not prevent them from predicting accurate energy levels. The key is to truncate the series calculated. These methods show a sort of false convergence such that if the series in them are truncated, they are still able to accurately calculate physically correct results.

c. Quantization for Irregular Classical Orbits

The only worker who has seriously investigated quantum states corresponding to irregular classical orbits is M. C. Gutzwiller,³ and the methods he has developed are entirely different from those discussed above. He suggests that progress can be made more easily by studying semiclassical approximations to the Green's function instead of the individual states. The Green's function $G(q, q'; E)$ is in semiclassical approximation related to the action integral evaluated on a classical path of energy E from q to q' :

$$G(q, q'; E) \approx \sum_{\substack{\text{classical} \\ \text{paths}}} A_n \exp [i S_n(q, q'; E) / \hbar] \quad (\text{II.73})$$

He shows that the "response function"

$$g(E) = \int G(q, q'; E) dq \quad (\text{II.74})$$

is determined primarily by the periodic orbits, and that it implicitly contains the entire energy spectrum,

$$g(E) = \sum_n (E - E_n)^{-1} \quad (II.75)$$

This does not say that individual quantum states are associated with individual periodic orbits, but only that the set of all periodic orbits contains information sufficient to determine approximately the set of quantum states.

The methods developed by Gutzwiller are not easy to implement, because of the difficulty of determining a sufficiently large set of periodic orbits. He carried out one (widely misunderstood) calculation on an anisotropic Kepler problem, but the results must be regarded as preliminary, and work on this problem is continuing.

No other methods have yet been proposed for this difficult problem.

d. Calculation of Invariant Toroids

We have discussed earlier the hypotheses advanced by Percival on the general nature of vibrational spectra. Besides this, Percival and Pomphrey^{4a,b} have suggested several methods for computing eigenvalues of a regular spectrum. Two significant general features of their methods are: 1) they can all be derived from a very general classical variational principle which is somewhat analogous to the standard quantum variational principle; 2) they deliberately avoid the calculation

of generating functions which may be complicated multiple-valued functions, and instead calculate the invariant toroids directly.

One of their proposed methods is as follows. Let us write the vector equations of motion for a two-dimensional oscillator in the form

$$\ddot{\vec{q}} = F(\vec{q}) \quad (\text{II.76})$$

with $F(\vec{q})$ consisting of both linear and non-linear terms,

$$F(\vec{q}) = -\vec{\lambda} \cdot \vec{q} + \vec{F}^{\text{anh}}(\vec{q}) \quad (\text{II.77})$$

Now if θ_1, θ_2 are the two angles that represent the position on the toroid, then the mapping from the forms into configuration space $\vec{q}(\theta_1, \theta_2)$ can be expanded in a Fourier series as

$$\vec{q}(\theta_1, \theta_2) = \sum_{s_1, s_2} q_{s_1, s_2} \exp i(s_1 \theta_1 + s_2 \theta_2) \quad (\text{II.78})$$

Since each θ varies linear with time,

$$\theta_i = \omega_i t + \delta_i \quad (\text{II.79})$$

When the expansion (II.78) is applied to the equation of motion (II.76) we obtain a set of non-linear algebraic equations for the coefficients q_{s_1, s_2} and the frequencies ω_1, ω_2 :

$$\begin{aligned} [\lambda_x - (s_1 \omega_1 + s_2 \omega_2)^2] X_{s_1, s_2} &= F_{x, s_1, s_2}^{\text{anh}} \\ [\lambda_y - (s_1 \omega_1 + s_2 \omega_2)^2] Y_{s_1, s_2} &= F_{y, s_1, s_2}^{\text{anh}} \end{aligned} \quad (\text{II.80})$$

where

$$\vec{F}_{s_1 s_2}^{\text{anh}} = (\omega\pi)^{-N} \int_{-\pi}^{\pi} \exp[-i(s_1\theta_1 + s_2\theta_2)] \vec{F}_{\frac{\omega}{g}}^{\text{anh}}(\theta_1, \theta_2) d\theta_1 d\theta_2$$

The only remaining problem is the solution to these algebraic equations (II.80); Percival and Pomphrey suggest several iterative methods for accomplishing this. All of the iterative methods begin from the solution to the harmonic problem:

$$s_1=1 \quad s_2=0 \quad \Rightarrow \quad \lambda_x = \omega_1^2 \quad x_{10} \text{ arbitrary}$$

$$s_1=0 \quad s_2=1 \quad \Rightarrow \quad \lambda_y = \omega_2^2 \quad y_{01} \text{ arbitrary}$$

In carrying out the iteration, certain variables can be specified arbitrarily. In the simplest method, we may hold x_{10} and y_{01} fixed throughout every step; then the frequencies and coefficients in each step are given by

$$\omega_1^2 = \lambda_x - F_{x_{10}}^{\text{anh}} / x_{10}$$

$$\omega_2^2 = \lambda_y - F_{y_{01}}^{\text{anh}} / y_{10}$$

$$x_{s_1 s_2} = F_{x_{s_1 s_2}}^{\text{anh}} / [\lambda_x - (s_1 \omega_1 + s_2 \omega_2)^2]$$

$$y_{s_1 s_2} = F_{y_{s_1 s_2}}^{\text{anh}} / [\lambda_y - (s_1 \omega_1 + s_2 \omega_2)^2]$$

Alternately, we may hold the frequencies fixed throughout every step, or, for quantization purposes, hold the action variables fixed at half-integers through every step. (This last method requires the relationship between the mapping $q(\theta_1, \theta_2)$ and the values of the action variables.)

It would be expected that some of these iteration methods would diverge in general, because of the presence of irregular motion; some however may show a useful false convergence, and Percival also suggests that the convergent iteration scheme of Arnold¹ may even be applied. Accurate results for some simple model systems have been obtained.

III. THE BIRKHOFF-GUSTAVSON NORMAL FORM

In this chapter we describe a method of treating nonseparable classical systems which was originally developed by Birkhoff⁷ and later extended by Gustavson.⁸ This method forms the central feature of our semiclassical quantization prescription since it provides the means of solving for the classical motion in preparation to applying the semiclassical quantization conditions. Birkhoff's method provides a procedure to transform the original nonseparable oscillator Hamiltonian into a normal form (to be defined presently) via a succession of canonical transformations. This normal form consists of a power series in one-dimensional harmonic oscillator Hamiltonians. Because of the particular simplicity of this final form, the Hamiltonian can be easily quantized, as we will discuss in the next chapter. But first, let us examine the purely classical aspects - the generation of the normal form.

The result obtained by Birkhoff is that, given a Hamiltonian H which can be written as a formal power series without constant or linear terms, and such that the quadratic terms may be written as a sum of uncoupled harmonic oscillator terms with incommensurable frequencies, then there exists a formal real canonical transformation generated by a power series, such that H is transformed into a Hamiltonian which is a power series in one-dimensional uncoupled harmonic oscillator Hamiltonians, i.e.

$$H \rightarrow \Gamma(\xi_1^2 + \eta_1^2, \dots, \xi_n^2 + \eta_n^2) \quad (\text{III.1})$$

where ξ_k are canonical coordinates, η_k are canonical momenta, and Γ is a formal power series in $\xi_k^2 + \eta_k^2$. (The constant term can always be eliminated by shifting the zero of energy. Linear terms can be eliminated in a nondissipative system. The quadratic terms must be positive definite in order to be written as harmonic oscillator terms. Formal power series are considered in order to avoid convergence considerations.) If the series Γ were to converge, the new equations could be easily integrated, and the transformation to angle-action variables would be straightforward. (This is carried out in an example later in this chapter.) Since the motion could be expressed in terms of angle-action variables, n independent isolating integrals would exist, and the original coordinates and momenta could be written as quasiperiodic functions.

Unfortunately, Siegel^{23,10b} has shown that Birkhoff's normal form diverges in general. That this should be so follows from the behavior of nonseparable systems of oscillators, as discussed in Chap. II. For cases in which irregular orbits can be found arbitrarily close to quasiperiodic orbits, the motion cannot be described continuously over a range of energies in terms of purely quasiperiodic solutions. But this is exactly what a convergent normal form would imply, since angle-action variables could be constructed. As discussed by Moser,^{10b} the

numerical difficulty which is responsible for the divergence of the normal form is the small divisor problem of celestial perturbation theory, which was mentioned earlier. (It may be pointed out that according to a result by Rüssman,^{24,10b} Birkhoff's normal form will converge for quasiperiodic systems, such as completely separable systems for example.)

Birkhoff's method was applied by Gustavson in order to obtain power series expressions for isolating integrals, and to analytically predict the Poincaré surfaces of section which Hénon and Heiles obtained. Since the potential treated had commensurable frequencies (equal, in fact), Gustavson had to modify Birkhoff's method somewhat, in order to obtain a kind of normal form. However, the isolating integrals which Gustavson derived were successful in reproducing the Poincaré surfaces of section of the H & H system, at least for the quasiperiodic cases. As expected, the method failed to predict the "random" scatter of points on the surface of section, which corresponds to irregular orbits.

The procedure for transforming to Birkhoff's normal form will be described here in detail for completeness sake, although it is an essentially unmodified form of the procedure presented in Gustavson's paper.⁸

Transformation to Normal Form

Let us consider a system described by a Hamiltonian

$$H(u, v) = H^{(2)}(u, v) + H^{(3)}(u, v) + \dots$$

which is a power series in coordinates u and momenta v . $H^{(s)}$ is taken to be a homogeneous polynomial of degree s .

$$H^{(s)}(u, v) = \sum_{\substack{i+j=s \\ i, j \geq 0}} a_{ij} u^i v^j \quad s = 2, 3, \dots$$

For systems in which $H^{(2)}$ is positive definite (i.e. cases for which $H^{(2)}$ represents a harmonic oscillator) then there exists a canonical transformation $(u, v) \rightarrow (q, p)$ which transforms $H^{(2)}$ into the form

$$H^{(2)}(q, p) = \sum_{k=1}^n \frac{\omega_k}{2} (q_k^2 + p_k^2) \quad (\text{III.2})$$

Following Gustavson, we now define a normal form. Let $H(q, p)$ be a Hamiltonian with $H^{(2)}(q, p)$ as given in Eq. III.2. Then we say that $H(q, p)$ is in normal form if $DH(q, p) = 0$, where

$$D = - \sum_{k=1}^n \omega_k \left(q_k \frac{\partial}{\partial p_k} - p_k \frac{\partial}{\partial q_k} \right) \quad (\text{III.3})$$

This is equivalent to requiring that the Poisson bracket of $H^{(2)}$ with H vanish, since D is given by

$$D = - [H^{(2)}, H] \quad (\text{III.4})$$

(The minus sign is included here to be consistent with the quantity he calls D; apparently his equation 2.4 should also have this minus sign.)

Using this definition for the normal form, we will now treat the two dimensional case which we studied. In this case $H^{(3)}$ is the only nonzero addition to the unperturbed Hamiltonian. However, the method can be applied to cases in which the original Hamiltonian is a power series truncated at any desired degree.

The Hamiltonian which we studied is given by

$$\begin{aligned} H &= \frac{1}{2} (p_1^2 + p_2^2 + \omega_1^2 q_1^2 + \omega_2^2 q_2^2) + \lambda q_2 (q_1^2 + \eta q_2^2) \\ &= H^{(2)} + H^{(3)} \end{aligned} \quad (\text{III.5})$$

where p is momentum, and q is coordinate. The unperturbed part $H^{(2)}$ of the Hamiltonian describes two uncoupled harmonic oscillators, while the perturbed part $H^{(3)}$ introduces a non-linear coupling. (This is the same Hamiltonian studied by Marcus, et al.^{1a,b} and Miller, et al.^{2a})

The second degree terms $H^{(2)}$ can be brought into Birkhoff's normal form by the transformation

$$\begin{aligned} p_k &\longrightarrow \omega_k^{1/2} p_k \\ q_k &\longrightarrow \omega_k^{-1/2} q_k \end{aligned} \quad (\text{III.6})$$

giving

$$H^{(2)} = \sum_{k=1}^2 \frac{1}{2} (p_k^2 + q_k^2) \omega_k \quad (\text{III.7})$$

$$H^{(3)} = \frac{\lambda}{\omega_1 \omega_2^{1/2}} q_1^2 q_2 + \frac{\lambda \eta}{\omega_2^{3/2}} q_2^3$$

This Hamiltonian (III.7) can now be transformed to normal form by a sequence of canonical transformations. Each transformation is defined by means of a type-2 generating function F_2 such that

$$F_2(P, q) = \sum_k P_k q_k + W^{(s)}(P, q) \quad (\text{III.8})$$

where P are the new canonical momenta and where the properties of $W^{(s)}$ will be described presently. (Where the abbreviated notation $P, Q, p,$ or q is used, it should be clear that P means $P_1, \dots, P_n,$ etc.) The first term on the right hand side of (III.8) is an identity generator; its purpose will be to leave the terms which are already in normal form unchanged. The transformation equations which result are

$$Q = q + \frac{\partial W^{(s)}}{\partial P} \quad (\text{III.9a})$$

$$p = P + \frac{\partial W^{(s)}}{\partial q} \quad (\text{III.9b})$$

$$H(p, q) = \Gamma(P, Q) \quad (\text{III.9c})$$

where Q is the coordinate canonically conjugate to P , and where Γ is the Hamiltonian in the new coordinates. Beginning with $s = 3$, the transformations sequentially normalize the terms of degree s in the Hamiltonian. As we will show, this can be achieved by taking $W^{(s)}$ to be a homogeneous polynomial of degree s .

Following the usual procedure of Appendix I for obtaining an equation for $W^{(s)}$, we substitute (III.9a,b) into (III.9c) to obtain

$$H\left(P + \frac{\partial W^{(s)}}{\partial q}, q\right) = \Gamma\left(P, q + \frac{\partial W^{(s)}}{\partial P}\right) \quad (\text{III.10})$$

Following Gustavson, if we expand H and Γ in a Taylor series about P and q , and then collect and equate all terms of equal degree, the following set of equations, equivalent to (III.10) results:

$$H^{(i)}(P, q) = \Gamma^{(i)}(P, q) \quad i < s \quad (\text{III.11a})$$

$$DW^{(s)}(P, q) = \Gamma^{(s)}(P, q) - H^{(s)}(P, q) \quad i = s \quad (\text{III.11b})$$

$$\Gamma^{(i)}(P, q) - H^{(i)}(P, q) + \sum_j \frac{1}{j!} \left[\left(\frac{\partial W^{(s)}}{\partial q} \right)^j \frac{\partial^{j|j|} H^{(i)}}{\partial P^j} - \left(\frac{\partial W^{(s)}}{\partial P} \right)^j \frac{\partial^{j|j|} \Gamma^{(i)}}{\partial q^j} \right] \quad i > s \quad (\text{III.11c})$$

$$l - |j| + |j|(s-1) = i$$

$$1 \leq |j| \leq l < i$$

$$l \geq 2 \quad s \geq 3$$

where $|j| = j_1! j_2!$. In these equations

$$H^{(i)}(P, q) = H^{(i)}(q, q) \Big|_{P=q} \quad (\text{III.12})$$

and

$$\Gamma^{(i)}(P, q) = \Gamma^{(i)}(P, Q) \Big|_{Q=q}$$

as arises from the Taylor expansion. Thus $H^{(1)}(P, q)$ effectively means $H^{(1)}(p, q)$ with p replaced by P and $\Gamma^{(1)}(P, q)$ means $\Gamma^{(1)}(p, q)$ with q replaced by q . In equation (III.11b), the operator D is given by eqn. (III.3).

Equation (III.11a) shows that the transformation of degree s leaves lower degree terms unaffected; (III.11b) is the equation to be solved for $W^{(s)}$, and when this is done, (III.11c) gives the higher degree terms in the new Hamiltonian. (For an example which may clarify the concise but somewhat opaque notion of eqn. III.11c, see Appendix IV.)

In order to solve equation (III.11b) for $W^{(s)}$, we temporarily make a transformation to variables in which D is diagonal: define

$$P_k = 2^{-1/2} (\eta_k + i \xi_k) \quad (\text{III.13a})$$

$$\xi_k = i 2^{1/2} (\eta_k - i \xi_k) \quad (\text{III.13b})$$

Under this transformation, $D \rightarrow \tilde{D}$ where

$$\tilde{D}(\eta, \xi) = i \sum_k \omega_k \left(\xi_k \frac{\partial}{\partial \xi_k} - \eta_k \frac{\partial}{\partial \eta_k} \right) \quad (\text{III.14})$$

It follows by inspection that functions of the form

$$\Phi_{\ell_1, \ell_2, m_1, m_2} = \eta_1^{\ell_1} \eta_2^{\ell_2} \xi_1^{m_1} \xi_2^{m_2} \quad (\text{III.15})$$

are eigenfunctions of \tilde{D} with eigenvalues

$$i \sum_k \omega_k (m_k - l_k)$$

i.e.

$$\tilde{D} \Phi_{l_1, l_2, m_1, m_2} = \left[i \sum_k \omega_k (m_k - l_k) \right] \Phi_{l_1, l_2, m_1, m_2} \quad (\text{III.16a})$$

Consequently

$$\tilde{D}^{-1} \Phi_{l_1, l_2, m_1, m_2} = \left[i \sum_k \omega_k (m_k - l_k) \right]^{-1} \Phi_{l_1, l_2, m_1, m_2} \quad (\text{III.16b})$$

Under the transformation discussed here, eqn. (III.11b) becomes

$$\tilde{D} \tilde{W}^{(s)} = \tilde{\Gamma}^{(s)} - \tilde{H}^{(s)} \quad (\text{III.17})$$

This equation may now be solved for $\tilde{W}^{(s)}$ operating with \tilde{D}^{-1} on both sides

$$\tilde{W}^{(s)} = \tilde{D}^{-1} \left[\tilde{\Gamma}^{(s)} - \tilde{H}^{(s)} \right] \quad (\text{III.18})$$

$\tilde{H}^{(s)}$ is a known function. But so far, $\tilde{\Gamma}^{(s)}$ has been unspecified. $\tilde{\Gamma}^{(s)}$ is now determined from the requirement that $\tilde{W}^{(s)}$ be finite. Clearly, $\tilde{\Gamma}^{(s)}$ must be chosen so as to exactly cancel any terms in $\tilde{H}^{(s)}$ which would give a vanishing denominator in eqn. (III.16b). So long as the frequencies are incommensurable, the only terms that must appear in $\tilde{\Gamma}^{(s)}$ are those for which $m_k = l_k$ for all k ; those terms are

$$(i\eta_1 \xi_1)^{m_1} (i\eta_2 \xi_2)^{m_2} = \left[\frac{1}{2} (P_1^2 + Q_1^2) \right]^{m_1} \left[\frac{1}{2} (P_2^2 + Q_2^2) \right]^{m_2} \quad (\text{III.19})$$

Such terms are called null space terms (because \tilde{D} operating on them gives a null result). The remaining terms are called range space terms.

Therefore, if $\tilde{H}^{(s)}$ is separated into null space terms $\tilde{N}^{(s)}$ and range space terms $\tilde{R}^{(s)}$,

$$\tilde{H}^{(s)} = \tilde{N}^{(s)} + \tilde{R}^{(s)} \quad (\text{III.20})$$

and if we require $\tilde{\Gamma}^{(s)}$ to cancel the null space terms in $H^{(s)}$, eqn. (III.18) results in:

$$\tilde{\Gamma}^{(s)} = \tilde{N}^{(s)} \quad (\text{III.21a})$$

$$\tilde{W}^{(s)} = \tilde{D}^{-1} [-\tilde{R}^{(s)}] \quad (\text{III.21b})$$

Having obtained $\tilde{\Gamma}^{(s)}$ and $\tilde{W}^{(s)}$, we can use the inverse equations to eqn. (III.13) to obtain $\Gamma^{(s)}$ and $W^{(s)}$. $\Gamma^{(s)}$ will be composed only of terms such as in eqn. (III.19) (as mentioned, provided that the frequencies ω_k were incommensurable.) Note that arbitrary null space terms could be added to W , but following Gustavson we omit such terms. The above method for constructing the normal form simultaneously satisfies

our definition of a normal form (paragraph containing eqn. III.3), and serves to eliminate exactly those terms in $H^{(3)}$ which would cause divergence of the equation for $W^{(s)}$ (eqn. III.18).

Now that degree s terms in the Hamiltonian have been transformed into the normal form $\Gamma^{(s)}$, $W^{(s)}$ must be used in eqn. (III.11c) to calculate higher degree terms in the new Hamiltonian. The process can then be repeated to normalize terms of degree $s + 1$. It will be found that the normal form will contain only terms of even degree.

As an example, the normal form obtained through degree four terms for the Hamiltonian (III.5), with

$$\begin{aligned} \omega_1 &= 1.3 & \lambda &= -0.1 \\ \omega_2 &= 0.7 & \eta &= 0.1 \end{aligned}$$

is given by:

$$\begin{aligned} \Gamma &= \frac{1}{2} \left\{ 1.3 (P_1^2 + Q_1^2) + 0.7 (P_2^2 + Q_2^2) \right\} \\ &\quad - 1.56185 \times 10^3 \left[\frac{1}{2} (P_2^2 + Q_2^2) \right]^2 \\ &\quad - 1.023323 \times 10^2 \left[\frac{1}{4} (P_2^2 + Q_2^2) (P_1^2 + Q_1^2) \right] \\ &\quad - 5.80199 \times 10^3 \left[\frac{1}{2} (P_1^2 + Q_1^2) \right] \end{aligned} \quad (\text{III.23})$$

Once the transformation to Birkhoff's normal form is made, the harmonic oscillator terms can be transformed to action variables via the canonical transformation

$$P_k = \sqrt{\frac{J_k}{\pi}} \cos 2\pi w_k \quad (\text{III.24a})$$

$$Q_k = \sqrt{\frac{J_k}{\pi}} \sin 2\pi w_k \quad (\text{III.24b})$$

which results in

$$\frac{1}{2} (P_k^2 + Q_k^2) = \frac{J_k}{2\pi} \quad (\text{III.25})$$

For the example just given, the normal form (eqn. III.23) becomes (through terms of degree four in (Q,P)):

$$\begin{aligned} \Gamma &= 1.3 \left(\frac{J_1}{2\pi} \right) + 0.7 \left(\frac{J_2}{2\pi} \right) \\ &\quad - 1.56185 \times 10^{-3} \left(\frac{J_2}{2\pi} \right)^2 \\ &\quad - 1.023323 \times 10^{-2} \left(\frac{J_1 J_2}{4\pi^2} \right) \\ &\quad - 5.80199 \times 10^{-3} \left(\frac{J_1}{2\pi} \right)^2 \end{aligned} \quad (\text{III.26})$$

As Chap. II showed, once the classical motion is expressed in terms of action variables, semiclassical quantization is straightforward. This is carried out in the next chapter. However, we must first deal with commensurable frequencies and their effect on the normal form.

So far, it has been assumed that the frequencies ω_k are incommensurable. To see what must be done in the commensurable case, consider the following: Assume that $\omega_1 = 2\omega_2$. Consider eqn(III.16a) for $\Phi_{1002} = \eta_1 \xi_2^2$

$$\begin{aligned} \tilde{D} \eta_1 \xi_2^2 &= [\omega_1(-1) + \omega_2(2)] \eta_1 \xi_2^2 \\ &= 0 \end{aligned} \quad (\text{III.27})$$

Therefore $\tilde{D}^{-1} \eta_1 \xi_2^2$ would diverge.

In order to avoid this occurrence, $\Gamma^{(n)}$ must be chosen to cancel such additional terms in $H^{(s)}$ for the commensurable case. Aside from this change, the procedure is identical to that for the incommensurable case.

The Hamiltonian which we treated is given by

$$H = \frac{1}{2} (p_1^2 + p_2^2) + \frac{1}{2} (g_1^2 + g_2^2) + \lambda g_2 (g_1^2 + \eta g_2^2) \quad (\text{III.28})$$

where

$$\lambda = \sqrt{.0125}$$

$$\eta = -\frac{1}{3}$$

(Recall that this is the same case as treated by Noid and Marcus^{1c} (Chap. II).) If the normal form is constructed, then through degree 4 terms, the following result is found:

$$\begin{aligned} \Gamma = & \frac{1}{2} [(P_1^2 + Q_1^2) + (P_2^2 + Q_2^2)] \\ & - 5.2083 \times 10^{-4} \left[\frac{1}{2} (P_2^2 + Q_2^2) \right]^2 \\ & + 4.1667 \times 10^{-4} \left[\frac{1}{4} (P_2^2 + Q_2^2)(P_1^2 + Q_1^2) \right] \\ & - 5.2083 \times 10^{-4} \left[\frac{1}{2} (P_1^2 + Q_1^2) \right]^2 \\ & - 3.6459 \times 10^{-4} \left[(P_2 P_1 + Q_2 Q_1)^2 - (P_2 Q_1 - Q_2 P_1)^2 \right] \end{aligned} \quad (\text{III.29})$$

Comparison with eqn. (III.23) for an incommensurable case shows that cross terms have entered for the commensurable case.

We now wish to express this normal form in terms of angle-action variables. If the transformation eqns. (III.24) are applied to this normal form, noting that

$$P_2 P_1 + Q_2 Q_1 = \cos [2\pi (\omega_1 - \omega_2)] \quad (\text{III.30})$$

$$P_2 Q_1 - Q_2 P_1 = \sin [2\pi (\omega_1 - \omega_2)] \quad (\text{III.31})$$

then the following result is obtained:

$$\begin{aligned} J = & \frac{1}{2\pi} (J_1 + J_2) \\ & - 5.2083 \times 10^{-4} \left(\frac{J_2}{2\pi}\right)^2 \\ & + 4.1667 \times 10^{-4} \left(\frac{J_1 J_2}{4\pi^2}\right) \\ & - 5.2083 \times 10^{-4} \left(\frac{J_1}{2\pi}\right)^2 \\ & - 3.6459 \times 10^{-4} \left(\frac{J_1 J_2}{\pi^2}\right) \cos [4\pi (\omega_1 - \omega_2)] \end{aligned} \quad (\text{III.32})$$

It can be seen that while the unperturbed terms depend only on the J's, the higher degree terms depend on the w's. Therefore eqns. III.24 do not result in a transformation to angle-action variables. However, the additional canonical transformation given by

$$\begin{aligned} J_2 &= \frac{1}{2} (J + J') & \omega_2 &= (\omega + \omega') \\ J_1 &= \frac{1}{2} (J - J') & \omega_1 &= (\omega - \omega') \end{aligned} \quad (\text{III.33})$$

will yield a form which is cyclic in w (i.e. w does not appear). It follows that the canonically conjugate momentum J is constant. This two-step process can be carried out in one step using the canonical transformation

$$P_2 = \sqrt{\frac{J+J'}{2\pi}} \cos [2\pi (\omega + \omega')] \quad (\text{III.34a})$$

$$Q_2 = \sqrt{\frac{J+J'}{2\pi}} \sin [2\pi (\omega + \omega')] \quad (\text{III.34b})$$

$$P_1 = \sqrt{\frac{J-J'}{2\pi}} \cos [2\pi (\omega - \omega')] \quad (\text{III.34c})$$

$$Q_1 = \sqrt{\frac{J-J'}{2\pi}} \sin [2\pi (\omega - \omega')] \quad (\text{III.34d})$$

It will be found that all orders of the normal form will be cyclic in the variable ω . The complete result, through degree 8 terms for the case which we treated is shown in eqn. (III.35)

$$\Gamma^{(2)} = \frac{J}{2\pi} \quad (\text{III.35a})$$

$$\begin{aligned} \Gamma^{(4)} = & -\frac{9.1146 \times 10^{-4}}{\pi^2} (J^2 - J'^2) \cos(8\pi \omega') \\ & - \frac{3.9063 \times 10^{-4}}{\pi^2} J^2 - \frac{9.1146 \times 10^{-4}}{\pi^2} J'^2 \end{aligned} \quad (\text{III.35b})$$

$$\begin{aligned} \Gamma^{(6)} = & \frac{4.7 \times 10^{-7}}{\pi^3} (J^3 - J J'^2) \cos(8\pi \omega') \\ & + \frac{1.139 \times 10^{-5}}{\pi^3} (J^2 J' - J'^3) \cos(8\pi \omega') \\ & - \frac{3.50 \times 10^{-6}}{\pi^3} J^3 + \frac{1.139 \times 10^{-5}}{\pi^3} J^2 J' \\ & + \frac{4.7 \times 10^{-7}}{\pi^3} J J'^2 - \frac{1.899 \times 10^{-5}}{\pi^3} J'^3 \end{aligned} \quad (\text{III.35c})$$

$$\begin{aligned}
\Gamma^{(8)} = & \frac{5.6 \times 10^{-8}}{\pi^4} (J^2 - J'^2)^2 \cos(16\pi w') \\
& - \frac{4.6 \times 10^{-8}}{\pi^4} J^4 \cos(8\pi w') \\
& + \frac{2.72 \times 10^{-7}}{\pi^4} J^2 J'^2 \cos(8\pi w') \\
& - \frac{2.26 \times 10^{-7}}{\pi^4} J'^4 \cos(8\pi w') \\
& + \frac{1.77 \times 10^{-7}}{\pi^4} (J^3 J' - J J'^3) \cos(8\pi w') \\
& - \frac{4.4 \times 10^{-8}}{\pi^4} J^4 \\
& + \frac{1.77 \times 10^{-7}}{\pi^4} J^3 J' \\
& - \frac{1.59 \times 10^{-7}}{\pi^4} J^2 J'^2 \\
& - \frac{2.96 \times 10^{-7}}{\pi^4} J J'^3 \\
& + \frac{1.69 \times 10^{-7}}{\pi^4} J'^4
\end{aligned} \tag{III.35d}$$

where $\Gamma^{(n)}$ corresponds to terms of degree 2 in (P,Q) etc.

We can show that J is an action variable by noting that

$$\oint \sum_n P_k dQ_k = J \tag{III.36}$$

where the phase integral is evaluated over a path in (Q,P) - space

generated by letting w increase by unity (bringing Q, P through one cycle) while holding (J', w') fixed. This follows by observing that

$$\begin{aligned} dQ_2 &= \sqrt{\frac{J+J'}{2\pi}} \cos [2\pi (w+w')] (2\pi dw) \\ dQ_1 &= \sqrt{\frac{J-J'}{2\pi}} \cos [2\pi (w-w')] (2\pi dw) \end{aligned} \quad (\text{III.37})$$

and by replacing P_1, P_2 by expressions given in eqn. III.34a,c.

However, J' is not an action variable, since w' appears in the Hamiltonian. We therefore see that for the commensurable case we have not been able to convert the normal form analytically into angle-action variables. Nevertheless we have made an important accomplishment by transforming one pair of the variables into angle-action form. In so doing, we have effectively reduced Γ to a single degree of freedom, since the action J can be regarded as a fixed parameter. This will allow us to quantize J directly, and satisfy the other quantization condition by numerically quantizing a one-dimensional phase integral.

There is one additional note in regard to generating the normal form. Although the method is straightforward in principle, even for a relatively simple Hamiltonian the algebraic manipulations involved can rapidly get out of hand. (For example, expanded through 8th degree, the many higher order terms of the Hamiltonian generated while constructing the normal form lead to intermediate forms for the Hamiltonian containing almost five hundred terms.) We found it most convenient to carry out the sequence of canonical transformations using MACSYMA,²⁵ a computer

language that permits analytical calculations. The calculation of the normal form for the incommensurable case required less than 4 minutes CPU time on a PDP 10 when done using single precision, and 24 minutes CPU time when done using extended precision. Calculations for the commensurable case took slightly more CPU time.

In this chapter we have defined Birkhoff's normal form, shown how it is generated, and demonstrated that it can be used to express the classical motion in terms of angle-action variables. This process completes the first (and more difficult) step in the semiclassical quantization prescription. The next chapter shows the results which we have obtained by quantizing the angle-action form of Birkhoff's normal form.

IV. QUANTIZING THE NORMAL FORM

In this chapter we will show the results obtained by quantizing Birkhoff's normal form. This method of semiclassical quantization provides the energy spectrum in the form of a power series in the quantum numbers.

Quantizing the incommensurable case is most straightforward. Since the normal form can be expressed entirely in terms of action variables, we merely have to replace those action variables by an appropriate multiple of h (half- or full-integral quantization). The result will be a power series in the quantum numbers which provides an energy value for all quantum levels.

The commensurable case is much less straightforward to quantize. Since we have been able to express the normal form in terms of one action variable, we can again quantize that action variable by replacing it by the appropriate multiple of h . As will be discussed shortly, the second quantum condition is provided by numerically evaluating and quantizing a phase integral.

Again it should be borne in mind that we are ignoring the full complexity of classical motion (i.e. the "ergodic" trajectories embedded among the quasiperiodic trajectories). Numerically speaking, we are ignoring the fact that the normal form does not converge. Nevertheless, by truncating the normal form, we are able to obtain remarkable agreement with quantum mechanics, as this chapter will show.

A. The Incommensurable Case

Now that we have obtained the normal form, and can express it in terms of action variables, quantization is straightforward for the incommensurable case. We merely have to make the following replacement:

$$\frac{1}{2} (P_k^2 + Q_k^2) \longrightarrow \frac{J_k}{2\pi} \longrightarrow (n_k + \frac{1}{2}) \hbar \quad (\text{IV.1})$$

where n_k is an integer, and is referred to as the quantum number.

Notice that half-integral quantization has been chosen here. Reference to eqns. III.24a,b shows that J_k is given by

$$J_k = \oint P_k dQ_k \quad (\text{IV.2})$$

(no sum)

where the phase integral is evaluated over a path generated by allowing the angle variable w_k to increase by unity (bringing Q_k, P_k through one cycle) while holding $w_{k'}, (k' \neq k)$ constant. In (Q,P) -space, the resultant path will have two turning points (zeros of $P_{k'}$), and $Q_{k'}$, and $P_{k'}, (k' \neq k)$ may vary, but must return to their original values without passing through a full cycle (otherwise w_k , would have increased by unity). Half-integral quantization therefore follows. Also in the unperturbed limit, the normal form simply describes two uncoupled harmonic oscillators, for which half-integral quantization is correct. The quantization for the perturbed case therefore reduces unchanged to the correct quantization in the unperturbed limit.

I will now specialize to the case which we treated. For the Hamiltonian (III.5), with parameters

$$\begin{aligned}\omega_1 &= 1.3 & \lambda &= -0.1 \\ \omega_2 &= 0.7 & \eta &= 0.1\end{aligned}$$

the quantized normal form is (up to harmonic oscillator terms of degree 8),

$$\begin{aligned}\Gamma((n_1 + \frac{1}{2})\hbar, (n_2 + \frac{1}{2})\hbar) &= 1.3(n_1 + \frac{1}{2}) + 0.7(n_2 + \frac{1}{2}) \\ &- .0015 \ 6185 (n_2 + \frac{1}{2})^2 \\ &- .0102 \ 3323 (n_1 + \frac{1}{2})(n_2 + \frac{1}{2}) \\ &- .0058 \ 0199 (n_1 + \frac{1}{2})^2 \\ &- .0000 \ 1092 (n_2 + \frac{1}{2})^3 \\ &- .0001 \ 7719 (n_1 + \frac{1}{2})(n_2 + \frac{1}{2})^2 \\ &- .0002 \ 7327 (n_1 + \frac{1}{2})^2(n_2 + \frac{1}{2}) \\ &- .0000 \ 8625 (n_1 + \frac{1}{2})^3 \\ &- .0000 \ 0013 (n_2 + \frac{1}{2})^4 \\ &- .0000 \ 0529 (n_1 + \frac{1}{2})(n_2 + \frac{1}{2})^3 \\ &- .0000 \ 1183 (n_1 + \frac{1}{2})^2(n_2 + \frac{1}{2})^2 \\ &- .0000 \ 1071 (n_1 + \frac{1}{2})^3(n_2 + \frac{1}{2}) \\ &- .0000 \ 0229 (n_1 + \frac{1}{2})^4\end{aligned}\tag{IV.3}$$

where $\hbar = 1$ here.

Table IV.1 compares the energy levels predicted by our method against quantum mechanical values calculated with a 30 x 30 (900 function) harmonic oscillator basis set. Two percentage errors are listed. The first, ΔE_{rel} , is the percent error of the correction to the unperturbed energy (i.e. $\Delta E_{rel} = \frac{E_{BNF} - E_{QM}}{E_0 - E_{QM}}$). This error parameter is a useful measure of the improvement that a semiclassical calculation gives over a zeroth order approximation which treats the system as a set of uncoupled harmonic oscillators. The second, ΔE_{abs} , is the percent error of the energy value ($\Delta E_{abs} = \frac{E_{BNF} - E_{QM}}{E_{QM}}$). As shown, ΔE_{rel} is less than 2% through level 42, and less than about 7% over the entire spectrum. ΔE_{abs} is less than about .08% through level 42, and less than about .5% over the entire spectrum.

It will be seen that the absolute error of the semiclassical value is comparable to the spacing between levels for states near the escape energy ($E_{esc} = 11.5$). For this reason, the correspondence between semiclassical energy values and quantum mechanical values is uncertain for some of the higher energy levels. States have been matched in order of ascending energy in the table.

Table IV.1. Energy Levels for an Incommensurable Case.

n	N_0	N_1	$E_{\text{BGNF}}^{(a)}$	$E_{\text{QM}}^{(b)}$	$E_0^{(c)}$	$\Delta E_{\text{rel}}^{(d)}$	$\Delta E_{\text{abs}}^{(e)}$
1	0	0	.9955	.9955	1.0000	0%	0%
2	0	1	1.6870	1.6870	1.7	0%	0%
3	1	0	2.2782	2.2781	2.3	.5%	.004%
4	0	2	2.3750	2.3750	2.4	0%	0%
5	1	1	2.9584	2.9584	3.0	0%	0%
6	0	3	3.0595	3.0596	3.1	-.2%	-.003%
7	2	0	3.5480	3.5479	3.6	.2%	.003%
8	1	2	3.6348	3.6347	3.7	.2%	.003%
9	0	4	3.7404	3.7404	3.8	0%	0%
10	2	1	4.2164	4.2162	4.3	.2%	.005%
11	1	3	4.3071	4.3069	4.4	.2%	.005%
12	0	5	4.4176	4.4176	4.5	0%	0%
13	3	0	4.8045	4.8043	4.9	.2%	.004%
14	2	2	4.8803	4.8799	5.0	.3%	.008%
15	1	4	4.9753	4.9749	5.1	.3%	.008%
16	0	6	5.0910	5.0909	5.2	.1%	.002%
17	3	1	5.4601	5.4597	5.6	.3%	.007%
18	2	3	5.5397	5.5390	5.7	.4%	.013%
19	1	5	5.6393	5.6385	5.8	.5%	.014%
20	0	7	5.7605	5.7601	5.9	.3%	.007%

n	N_0	N_1	E_{BGNF}	E_{QM}	E_0	ΔE_{rel}	ΔE_{abs}
21	4	0	6.0468	6.0463	6.2	.3%	.008%
22	3	2	6.1108	6.1099	6.3	.5%	.015%
23	2	4	6.1944	6.1931	6.4	.6%	.021%
24	1	6	6.2989	6.2975	6.5	.7%	.022%
25	0	8	6.4260	6.4253	6.6	.5%	.012%
26	4	1	6.6889	6.6878	6.9	.5%	.016%
27	3	3	6.7564	6.7546	7.0	.7%	.027%
28	2	5	6.8443	6.8419	7.1	.9%	.035%
29	1	7	6.9540	6.9515	7.2	1.0%	.036%
30	0	9	7.0873	7.0861	7.3	.6%	.017%
31	5	0	7.2742	7.2730	7.5	.5%	.017%
32	4	2	7.3255	7.3234	7.6	.7%	.029%
33	3	4	7.3967	7.3935	7.7	1.0%	.043%
34	2	6	7.4891	7.4850	7.8	1.3%	.055%
35	1	8	7.6044	7.6003	7.9	1.6%	.054%
36	0	10	7.7445	7.7423	8.0	.9%	.028%
37	5	1	7.9019	7.8996	8.2	.8%	.029%
38	4	3	7.9564	7.9524	8.3	1.2%	.050%
39	3	5	8.0315	8.0259	8.4	1.5%	.070%
40	2	7	8.1288	8.1220	8.5	1.8%	.084%
41	1	9	8.2500	8.2435	8.6	1.8%	.079%
42	0	11	8.3973	8.3939	8.7	1.1%	.041%

n	N_0	N_1	E_{BGNF}	E_{QM}	E_0	ΔE_{rel}	ΔE_{abs}
43	6	0	8.4858	8.4835	8.8	.7%	.062%
44	5	2	8.5235	8.5190	8.9	1.2%	.053%
45	4	4	8.5814	8.5743	9.0	1.7%	.083%
46	3	6	8.6607	8.6513	9.1	2.1%	.109%
47	2	8	8.7632	8.7524	9.2	2.4%	.123%
48	1	10	8.8908	8.8805	9.3	2.5%	.116%
49	0	12	9.0456	9.0403	9.4	1.5%	.059%
50	6	1	9.0982	9.0934	9.5	1.2%	.053%
51	5	3	9.1387	9.1305	9.6	1.7%	.090%
52	4	5	9.2001	9.1882	9.7	2.3%	.130%
53	3	7	9.2840	9.2689	9.8	2.8%	.163%
54	2	9	9.3921	9.3752	9.9	3.2%	.180%
55	1	11	9.5264	9.5108	10.0	3.2%	.164%
57	0	13	9.6894	9.6812	10.1	2.0%	.085%
56	7	0	9.6808	9.6762	10.1	1.0%	.048%
58	6	2	9.7038	9.6948	10.2	1.8%	.093%
59	5	4	9.7472	9.7331	10.3	2.5%	.145%
60	4	6	9.8125	9.7932	10.4	3.2%	.197%
61	3	8	9.9012	9.8776	10.5	3.8%	.24%
62	2	10	10.0152	9.9895	10.6	4.2%	.26%
63	1	12	10.1568	10.1332	10.7	4.1%	.23%
66	0	14	10.3285	10.3161	10.8	2.6%	.120%

n	N_0	N_1	E_{BGNF}	E_{QM}	E_0	ΔE_{rel}	ΔE_{abs}
64	7	1	10.2769	10.2676	10.8	1.7%	.091%
65	6	3	10.3023	10.2861	10.9	2.6%	.157%
67	5	5	10.3489	10.3253	11.0	3.5%	.23%
68	4	7	10.4183	10.3877	11.1	4.3%	.29%
69	3	9	10.5121	10.4758	11.2	5.0%	.35%
70	2	11	10.6326	10.5937	11.3	5.5%	.37%
71	1	13	10.7819	10.7463	11.4	5.4%	.33%
76	0	15	10.9627	10.9439	11.5	3.4%	.172%
72	8	0	10.8582	10.8478	11.4	1.9%	.096%
73	7	2	10.8654	10.8493	11.5	2.5%	.148%
74	6	4	10.8933	10.8657	11.6	3.8%	.25%
75	5	6	10.9434	10.9053	11.7	4.8%	.35%
77	4	8	11.0172	10.9700	11.8	5.7%	.43%
78	3	10	11.1166	11.0612	11.9	6.6%	.50%
79	2	12	11.2439	11.1856	12.0	7.2%	.52%
80	1	14	11.4014	11.3484	12.1	7.1%	.47%
85	0	16	11.5902 ^f	11.5324 ^f	12.2		
81	8	1	11.4369	11.4129	12.1	3.5%	.21%
82	7	3	11.4460	11.4158	12.2	3.9%	.26%
83	6	5	11.4767	11.4325	12.3	5.1%	.39%
84	5	7	11.5305 ^f	11.4703	12.4		

a) Calculated using present method.

b) Calculated by Don Noid. 1f

c) Energy of uncoupled system

$$d) \Delta E_{\text{rel}} = \frac{E_{\text{BGNF}} - E_{\text{QM}}}{E_0 - E_{\text{QM}}}$$

$$e) \Delta E_{\text{abs}} = \frac{E_{\text{BGNF}} - E_{\text{QM}}}{E_{\text{QM}}}$$

f) Exceeds escape energy $E_{\text{esc}} = 11.5$

B. The Commensurable Case

For the commensurable case, we showed in the last chapter that the normal form can be written in terms of one action variable (J) and a canonically conjugate momentum and coordinate (J', w'). Therefore in order to quantize the normal form given in eqn III.35 let us begin by quantizing J . As eqn. III.36 states

$$J = \oint_c \sum_k P_k dQ_k \quad (\text{III.36})$$

where the path c is defined by letting the angle variable w increase by unity, holding w' fixed. In this case there appears to be no obvious argument telling how many caustics such an integration path will touch. We therefore found it necessary to obtain the correct quantization by considering a special case, and numerically generating an integration path using eqns. III.34. (This illustrates a problem with methods which do not display integration paths; the proper quantization sometimes can be determined only by actually counting the number of caustics touched by the integration path.) The commensurable case which we studied is that described by the Hamiltonian in eqn. III.28. Recall that this is the same commensurable case studied by Noid and Marcus.^{1c} Since the arguments which we must use to describe our treatment of this case are quite intricate, the reader will find it helpful to refer to the description of this case which was presented in Chap. II.

As discussed there, two classes of motion are found - rotations and librations. For both classes, for the half-dozen or so plots we generated numerically, the integration path touched four caustics. Keller's quantization prescription therefore requires full integral quantization.

$$J = (n+1) h \quad (\text{IV.4})$$

For an example of the integration path generated, see Fig. IV.1a,b. It will be noted that in the unperturbed limit, the normal form again represents two uncoupled harmonic oscillators (with equal frequencies in this case). The correct quantization is half-integral for each oscillator; however, because the frequencies are equal, the quantization for each oscillator can be directly added, yielding eqn. IV.4. We therefore find that the quantization for the perturbed case again reduces unchanged to the correct quantization in the unperturbed limit.

So far, we have only one quantum condition, and we need a second. We choose to quantize the phase integral

$$\oint_{c'} J' dw' = \oint_{c'} \sum_k P_k dQ_k \quad (\text{IV.5})$$

where the path c' is defined by allowing w' to vary over one cycle, holding w fixed. In order to obtain the correct quantization, we must determine how many caustics the integration path touches.

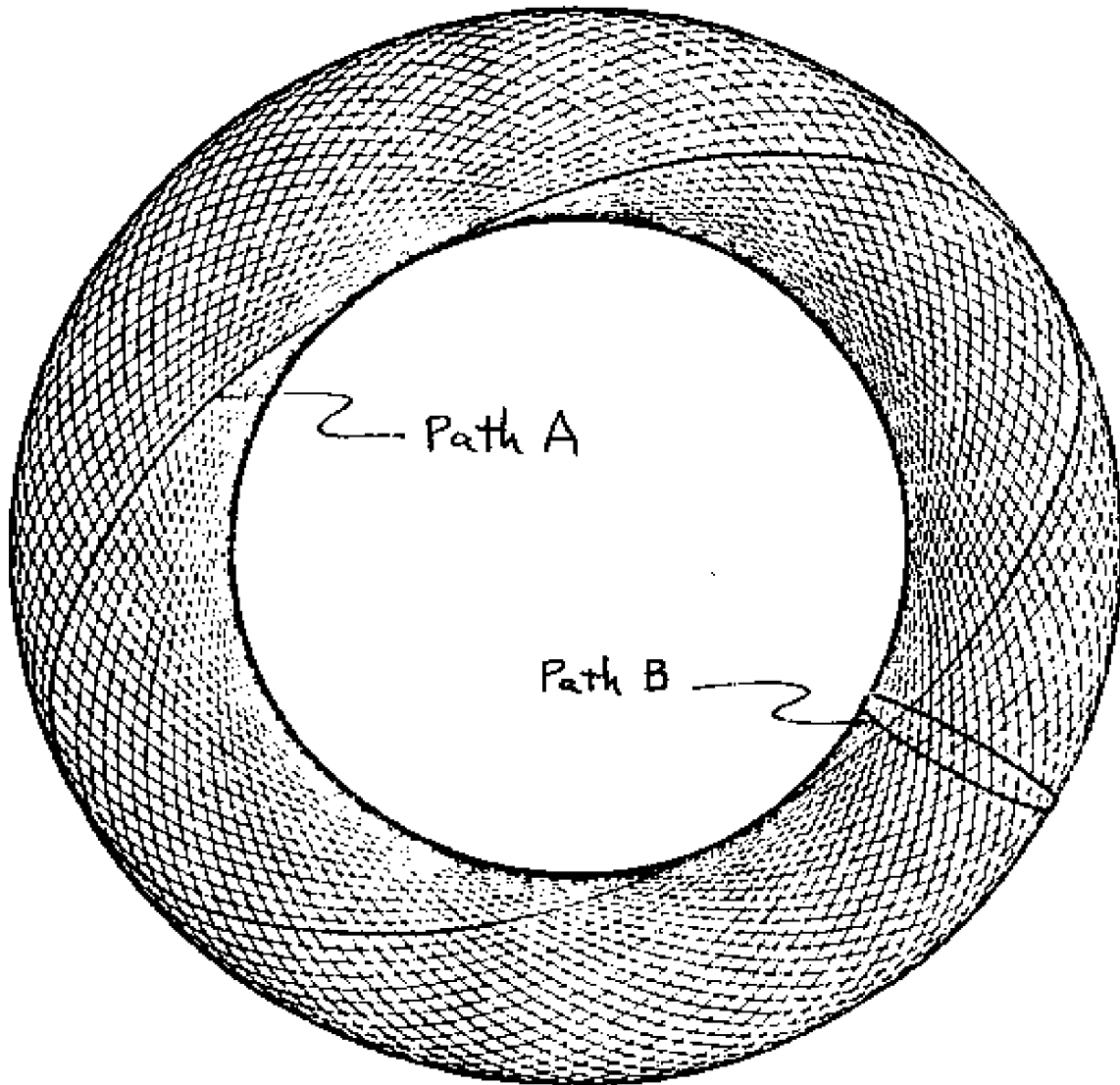


Fig. IV.1. Rotation Trajectory

Path A is generated by varying w , holding w' fixed

Path B is generated by varying w' , holding w fixed

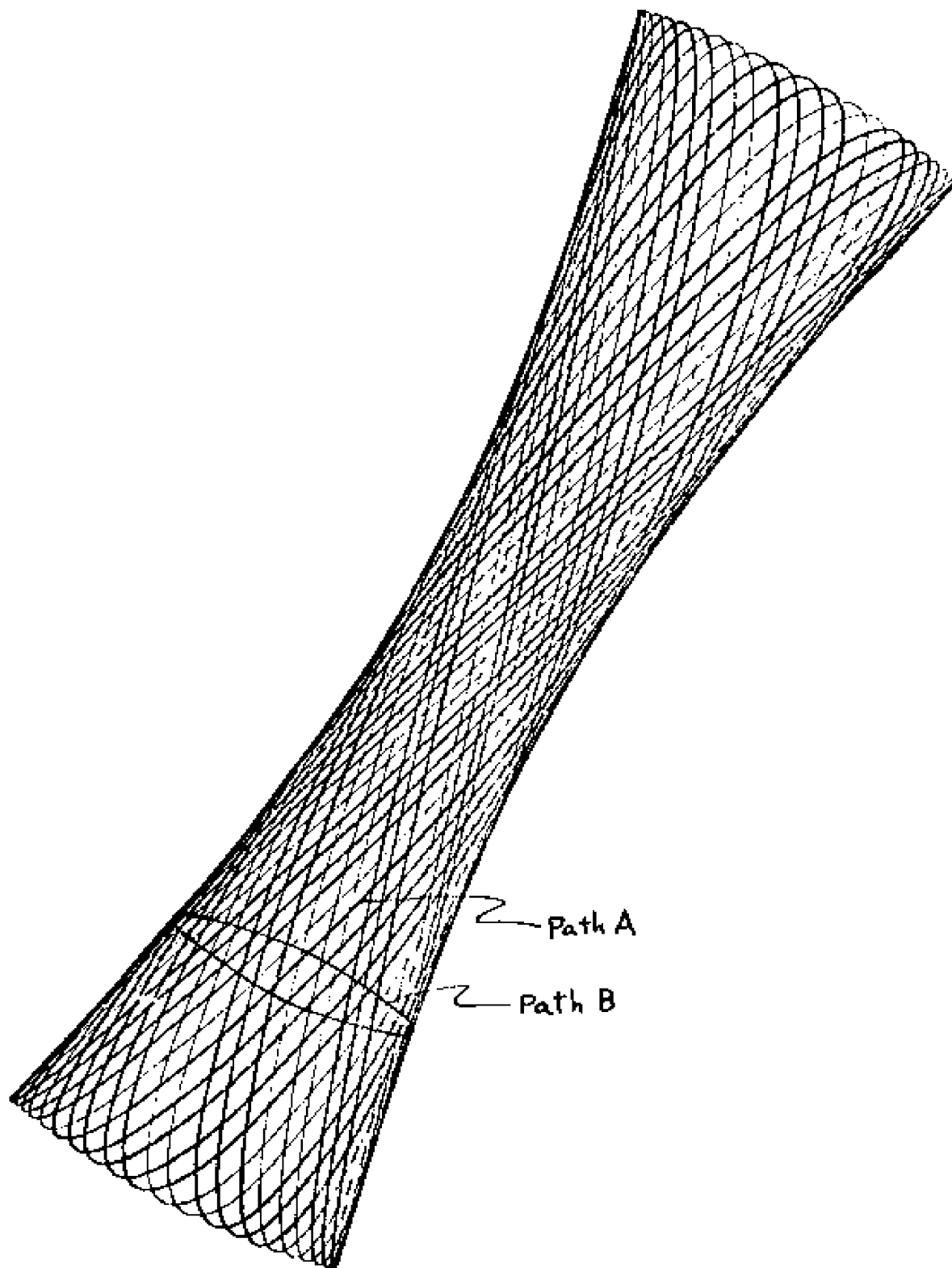


Fig. IV.2. Libration Trajectory

Path A is generated by varying w , holding w' fixed

Path B is generated by varying w' , holding w fixed

In order to do this, we again resort to considering our special case, and use eqns. III.34 in order to generate an integration path in (Q,P) - space as w' varies. The process is, however, complicated by the fact that J' varies with w' . In order to find the dependence of J' on w' , we use the normal form III.35. If the value of \bar{H} (energy) and J are chosen, eqn. III.35 can be solved for J' as a function of w' .

Care must be taken at this point. Notice that if \bar{H} were approximated by including terms only through $\bar{H}^{(6)}$, then a cubic equation for J' would result; if terms through $\bar{H}^{(8)}$ were included, then a quartic equation would result, and so on. We expect that as more terms of \bar{H} are included, J' will be expressed more accurately as a function of w' . But also an additional root is introduced for each additional degree we include in \bar{H} . Some roots will therefore be non-physical. In order to generate our integration path in (Q,P)-space, we must be able to select the correct root. We are looking for the roots whose value we know approximately when only lower degree terms are included in \bar{H} , and whose accuracy increases as we include higher degree terms in \bar{H} .

It was found by inspection that if terms through $\bar{H}^{(6)}$ are included, the roots to the resulting cubic equation for J' , as a function of w' , have a structure such as that shown in Figures IV.3 and IV.4 (with $w = 0$).

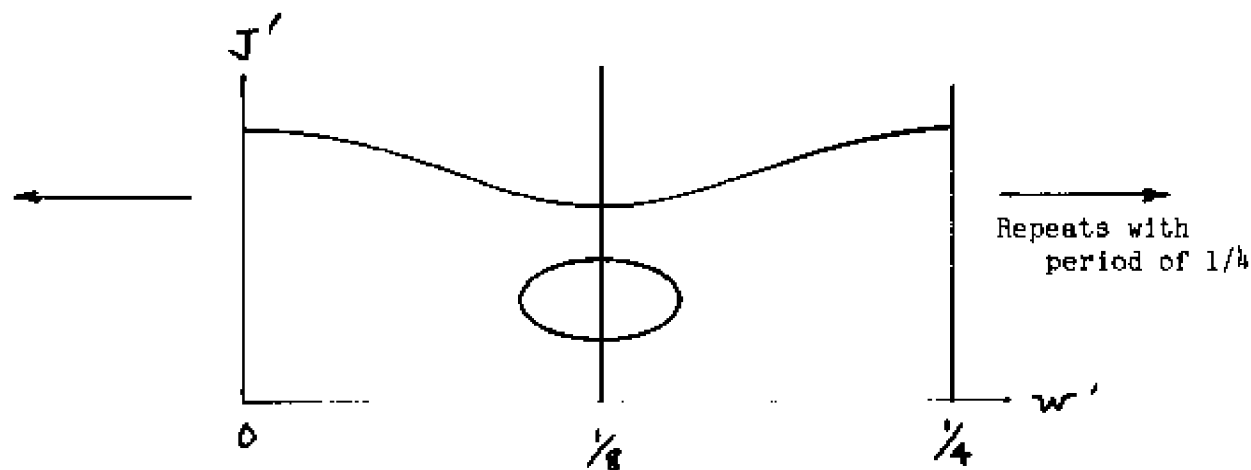


Fig. IV.3. Roots for a Rotation Case

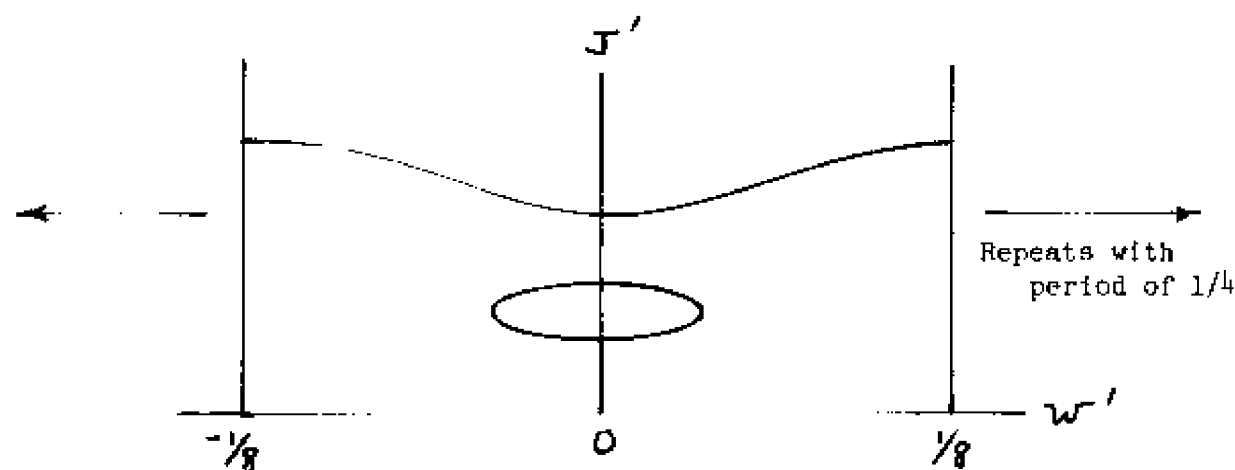


Fig. IV.4. Roots for a Libration Case

It can be seen that for some values of w' there is only one real root J' , while for other w' there are 3 real roots J' . (The root which is shown as a wavy line in the diagrams may appear above or below the closed loop.)

It was further found by investigation that if terms in through $\Gamma^{(8)}$ are included, then the roots lying on the closed loops of Figs. IV.3 and IV.4 only change slightly. The other root may change considerably, and a fourth root is also introduced since the equation for J' is now quartic.

Finally, when trajectories in (P,Q)-space were generated, and points on those trajectories were transformed into (J',w') variables, they were always found to lie on the loops shown in Figs. IV.3 and IV.4. Therefore it was concluded that they were the physically meaningful roots. The fact that the position of the closed loop changed only slightly when $\Gamma^{(8)}$ terms were included was taken as an indication that the series Γ had fairly good convergence.

One final point was observed: for the half-dozen or so cases tested, rotation cases always transformed onto a loop centered on $w' = 1/8$ (Fig. IV.3), while libration cases always transformed onto a loop centered on $w' = 0$ (Fig. IV.4). Therefore integration paths in (Q,P)-space for rotation cases were generated by varying w' over a loop centered on $w' = 1/8$, while paths for libration cases were generated by varying w' over a loop centered on $w' = 0$.

Having determined which root J' was the correct one to choose, we proceeded to see how many caustics were touched by the integration path for the phase integral (IV.5). i.e. w' was varied over a cycle, the corresponding J' was calculated by choosing the correct root of $\Gamma = E$, and the transformation equations (III.34) were used to generate an integration path. This path is shown (labeled as Path B) lying on top of a trajectory in Figs. IV.1 and IV.2.

Using Marcus's notation, we see by referring to Figs. IV.1 and IV.2 that integrating around a loop centered on $w' = 1/8$ for a rotation

case is topologically equivalent to calculating an r -cycle phase integral.

$$\oint_{\text{relation}} J' dw' = \oint p_r dr = (n_r + \frac{1}{2}) h \quad (\text{IV.6})$$

Integrating around a loop centered on $w' = 0$ for a libration case is topologically equivalent to calculating a θ -cycle phase integral

$$\oint_{\text{libration}} J' dw' = \oint p_y dy = \frac{1}{3} 2\pi \ell h \quad (\text{IV.7})$$

(where we have used the same quantization for the θ -cycle phase integral as Marcus did, despite the fact that a proper treatment requires that tunneling be included - as discussed earlier). Notice that in effect, the integration quantizes the area of the loops shown in Figs. IV.3 and IV.4.

Table IV.2. Energy Levels for a Commensurable Case

n_{QM}	l	n	n_r	$E_O^{(a)}$	$E_{QM}^{(b)}$	$E_{N\&M}^{(c)}$	$E_{BGNF}^{(d)}$	$\Delta E_{rel}^{(e)}$	$\Delta E_{abs}^{(f)}$
1	0	0	0	1.0	.9986	.9947	.9947	-279%	-.4%
2,3	<u>+1</u>	1	0	2.0	1.9901	1.9863	1.9862	- 39%	-.2%
4	0	2	1	3.0	2.9562	2.9506	2.9506	- 13%	-.2%
5,6	<u>+2</u>	2	0	3.0	2.9853	2.9815	2.9814	- 27%	0.13%
7,8	<u>+1</u>	3	1	4.0	3.9260	3.9233	3.9226	- 5%	-.09%
9	<u>+3</u>	3	0	4.0	3.9824	3.9803	3.9801	- 25%	-.10%
10					3.9858				
11	0	4	2	5.0	4.8702	4.8573	4.8577	- 10%	-.3%
12,13	<u>+2</u>	4	1	5.0	4.8987	4.9854	4.8954	- 3%	-.07%
14,15	<u>+4</u>	4	0	5.0	4.9863	4.9821	4.9821	- 31%	-.08%
16,17	<u>+1</u>	5	2	6.0	5.8170	5.816			
18	<u>+3</u>	5	1	6.0	5.8670	5.8713	5.8711	- 2%	-.05%
19					5.8815				
20,21	<u>+5</u>	5	0	6.0	5.9913	5.9869	5.9871	- 48%	-.07%
22	0	6	3	7.0	6.7379	6.7078	6.7098	- 11%	-.4%
23,24	<u>+2</u>	6	2	7.0	6.7649	6.7709	6.7668	1%	+0.03%
25,26	<u>+4</u>	6	1	7.0	6.8354	6.8500	6.8492	8%	+0.2%
27	<u>+6</u>	6	0	7.0	6.9989	6.9958	6.9951	-482%	-.05%
28					6.9994				
29,30	<u>+1</u>	7	3	8.0	7.6595	7.655			
31	<u>+3</u>	7	2	8.0	7.6977	7.7178	7.7184	.4%	.01%
32					7.7369				
33,34	<u>+5</u>	7	1	8.0	7.8327	7.8289	7.8293	- 2%	-.04%

n_{QM}	ℓ	n	n_r	E_0	E_{QM}	$E_{N\&M}$	E_{BGNF}	ΔE_{rel}	ΔE_{abs}
35,36	± 7	7	0	8.0	8.0094	8.0054	8.0058	38%	-.04%
37	0	8	4	9.0	8.5541	8.4919	8.5003	- 12%	-.6%
38,39	± 2	8	3	9.0	8.5764				
40,41	± 4	8	2	9.0	8.6779		8.6717	- 2%	-.07%
42 43	± 6	8	1	9.0	8.8113 8.8152	8.8084	8.8112	- 1%	-.02%
44,45	± 8	8	0	9.0	9.0217	9.0151	9.0192	12%	-.03%
46,47	± 1	9	4	10	9.444				
48 49	± 3	9	3	10	9.467 9.552				
50,51	± 5	9	2	10	9.629		9.626	- .8%	-.03%
52,53	± 7	9	1	10	9.794		9.794	0%	0%
54 55	± 9	9	0	10	10.035 10.036		10.035	1%	-.005%
56	0	10	5	11	10.305		10.221	- 12%	-0.8%
57,58	± 2	10	4	11	10.318				
59,60	± 4	10	3	11	10.463		10.455	- 1%	-.08%
61 62	± 6	10	2	11	10.573 10.590		10.581	- .1%	-.005%
63,64	± 8	10	1	11	10.774		10.779	2%	.05%
65,66	± 10	10	0	11	11.050		11.053	- 6%	.03%
67,68	± 1	11	5	12	11.152				
69 70	± 3	11	4	12	11.160 11.325				
71,72	± 5	11	3	12	11.383		11.383	0%	0%
73,74	± 7	11	2	12	11.534		11.536	.4%	.02%

n_{QM}	l	n	n_r	E_0	E_{QM}	$E_{N\&M}$	E_{BGNF}	ΔE_{rel}	ΔE_{abs}
75					11.750				
75	<u>+9</u>	11	1	12	11.752		11.764	5%	.11%
78,79	<u>+11</u>	11	0	12	11.968		12.074	331%	.9%
77	0	12	6	13	11.966		11.864	- 10%	-.9%
80,81	<u>+2</u>	12	5	13	12.065				
82,83	<u>+4</u>	12	4	13	12.206				
84					12.277				
85	<u>+6</u>	12	3	13	12.334		12.310	.6%	.04%
86,87	<u>+8</u>	12	2	13	12.480		12.491	2%	.09%
88,89	<u>+10</u>	12	1	13	12.712		12.750	13%	.3%
94					13.077				
97	<u>+12</u>	12	0	13	13.087		13.097	- 18%	.1%
91,92	<u>+1</u>	13	6	14	12.762				
90					12.748				
93	<u>+3</u>	13	5	14	13.032				
95,96	<u>+5</u>	13	4	14	13.081				
98,99	<u>+7</u>	13	3	14	13.233				

a) Energy of uncoupled system.

b) Calculated by Don Noid.^{1f}

c) Results of 1c.

d) Calculated using present method including terms through Γ (8)

$$e) \Delta E_{rel} = \frac{E_{BGNF} - E_{QM}}{E_0 - E_{QM}}$$

$$f) \Delta E_{abs} = \frac{E_{BGNF} - E_{QM}}{E_{QM}}$$

Let us now summarize the results which we have found so far for the commensurable case. We have shown that the physically meaningful integration paths in (J',w') -space are the loops shown in Figs. IV.3 and IV.4. Loops centered on $w' = 1/8$ map onto rotation cases in (Q,P) -space, and loops centered on $w' = 0$ map onto libration cases. We have plotted the integration paths in (Q,P) -space which are generated by the closed loop paths in (J',w') -space. Finally, we have used this information to determine an appropriate formula for quantizing the area of the closed loops.

With this preparation, the quantization process is relatively straightforward. Energy levels must be generated one at a time by numerically quantizing the phase integral given in eqn. IV.5. The process is similar to that used by Eastes, Noid, and Marcus (Chap. II), except it is greatly simplified because we have to satisfy only one quantum condition numerically. The other is satisfied analytically by quantizing the action variable J . Also, they had to numerically integrate the trajectory in order to generate two independent curvilinear surfaces of section which provided integration paths for the evaluation of two phase integrals. We eliminate the need to generate a trajectory, and we obtain an integration path for the phase integral by inverting the equation for the normal form, yielding J' as a function of w' , J , and E .

The energy levels were generated using a program written in APL. The steps involved in calculating one energy level are:

- 1) set J by selecting a value for the quantum number n in eqn. IV.4,
- 2) guess a value for the energy E (the energy of the unperturbed level is a good first guess),
- 3) calculate the phase integral shown in eqn. IV.5 numerically using values for J' provided by inverting the equation for Γ ,
- 4) iterate steps 2) through 4) until the value of the phase integral has converged with sufficient precision to the desired value.

The successive guesses for energy are made using a linear extrapolator. Two passes must be made initially in order to extrapolate. The processes converged fairly rapidly for the levels we calculated; a total of five to six passes were required for convergence.

Table IV.2 lists the levels calculated using this method for the commensurable case with Hamiltonian III.28 (normal form (III.35)). Comparison is made with semiclassical^{1c} and quantum^{1c,1f} levels of Noid and Marcus. The percentage error ΔE_{rel} in the correction to the unperturbed energy is in general somewhat higher than it was for the previous incommensurable case, and for certain levels it is very large. However, as indicated by the percentage error ΔE_{abs} , the absolute error of these levels is no worse on the average than that of other levels listed. Comparison with the results for the previous incommensurable case shows that ΔE_{abs} is roughly the same in both cases for the higher energy levels, but that ΔE_{abs} is much lower in the incommensurable case for the lower energy levels.

We also see in table IV.2 that the present semiclassical method has succeeded in accurately predicting many energy levels well beyond

the energy of transition to predominantly irregular behavior ($E_{\text{trans}} \approx 9$). These results are relevant to Percival's speculations on the existence on an irregular spectrum. First, we see that of the 29 levels with energies between the transition energy (≈ 9.0) and escape energy (13.33) 17 are calculated with reasonable accuracy by the 4th degree normal form.

For certain states having low values of ℓ (for example $\ell = \pm 1$, $n = 0$, $n_r = 4$) the present method gives no quantum level, because no conditions were found for which the phase integral (IV.5) satisfied the quantum condition (though in some such cases the quantum condition could be approximately satisfied.) Two possible explanations are: (i) that this results from errors intrinsic in the truncation of the normal form or (ii) that this results from the use of improper quantization conditions (the conditions used do not properly account for tunneling, which may be important for librations.) It should not be suggested that these levels belong to the irregular spectrum, because they fall into the pattern established by the regular spectrum.

There remain ten quantum states ($n_{\text{QM}} = 90-99$) for which the interpretation is uncertain. Those are listed in order of increasing energy, and quantum numbers are tentatively assigned to them by following the pattern of the lower states. (The assignment of $n_r = 13$, $\ell = \pm 3$ to states 90 and 93 and $n_r = 12$, $\ell = \pm 12$ to states 94 and 97 may appear to violate the non-crossing rule; this is not in fact a violation, however, because the states which avoid crossing interchange their character.) We cannot be sure that the assignments given are correct

(or even that a unique assignment is possible), but on the other hand, we have found no states which definitely fall outside of a regular pattern.

Let us now compare the methods used for the incommensurable case, and the commensurable case. In the incommensurable case, the energy levels are determined exclusively through analytical methods. A single calculation of the normal form supplies a value for all levels. In the commensurable case, the energy levels are determined partially through analytical methods, and partially through numerical methods. The calculation of the normal form is not enough; while one quantum condition is supplied analytically, the other must be supplied by quantizing a phase integral numerically. Once the correct root J' is determined, the correct cycle for w' is determined, and the correct quantization is determined, the process of generating the energy spectrum is straightforward.

V. CONCLUSION

In this section, we summarize the work accomplished here, compare the methods developed with others that are presently available, and consider possible extensions and applications of the theory.

A. Summary

We have presented a semiclassical method for approximating the Schrödinger equation, primarily for nonseparable systems. As such, it involves two steps - solving the classical problem, and quantizing. In this case, we solve the classical problem through a sequence of canonical transformations which transform the Hamiltonian into Birkhoff's normal form. Two cases arise. Taking the zero order solution to be that of a system of harmonic oscillators, we find that if the frequencies of the zero-order Hamiltonian are incommensurable, then the normal form can be written as a sum of products of one-dimensional harmonic oscillator Hamiltonians; if the frequencies of the zero-order Hamiltonian are commensurable, then additional terms which cannot be written as products of one-dimensional harmonic oscillator Hamiltonians enter into the normal form. The normal form in the incommensurable case can be quantized analytically to provide a simple formula for all the energy levels. In the commensurable case, one degree of freedom can be quantized

analytically, and the other is quantized numerically by a one-dimensional phase integration. Consequently, a simple formula for the entire energy spectrum is not obtained, and each energy level must be generated individually; the numerical effort involved is typical of one-dimensional WKB methods, though somewhat complicated by the fact that the new Hamiltonian

\bar{H} is not quadratic in the new momentum J' . Despite the fact that the method ignores any consideration of irregular classical motion, it predicts energy levels in excellent agreement with quantum mechanical calculations.

B. Comparisons

Let us begin by comparing the present method against other recently developed semiclassical techniques. Most of these have been numerical in nature. As such, they have required that the energy levels be generated one at a time. This usually involves a succession of iterations in order to generate each level. The present method also requires a succession of operations, but they need only be done once. After that, the normal form is known and, at least in the incommensurable case, the entire energy spectrum is known. Even in the commensurable case, the normal form technique has advantages. Although the levels must be calculated individually, fewer quantum conditions must be satisfied numerically. This could be a great advantage.

If we compare the present method with that developed by Born, we find that they have many things in common. Both are semiclassical.

Both supply the entire energy spectrum in the form of a simple formula, and furthermore, that formula is in the form of a power series in the quantum numbers in both cases.

Born's method is not limited to a harmonic oscillator Hamiltonian in zero order. But although Birkhoff specifies that his method requires a harmonic oscillator Hamiltonian in zero order, we suspect that the method could be generalized to include other choices - as long as the zero order case is integrable. For example a Morse oscillator might be a possible choice. The major step in the process of calculating the normal form is in finding a transformation to variables in which the operator D (eqn. III.4) is diagonal. This was possible in our case because of the special nature of the zero order Hamiltonian. Nevertheless if this step is accomplished, perhaps an analogous normal form could be constructed.

Now that we have listed the similarities between Born's and the present method let us list the differences. In effect, the methods do things in a different order. Both begin with the original classical variables, but Born first transforms to angle-action variables of the unperturbed problem, and then transforms to the proper angle-action variables for the perturbed problem via a succession of canonical transformations. In the present method, we transform from the original variables via a succession of canonical transformations to Birkhoff's normal form. Then we make a trivial transformation to the angle-action variables of the perturbed problem. Having reached the same point, both methods quantize the action variables according to the semiclassical quantization prescription in

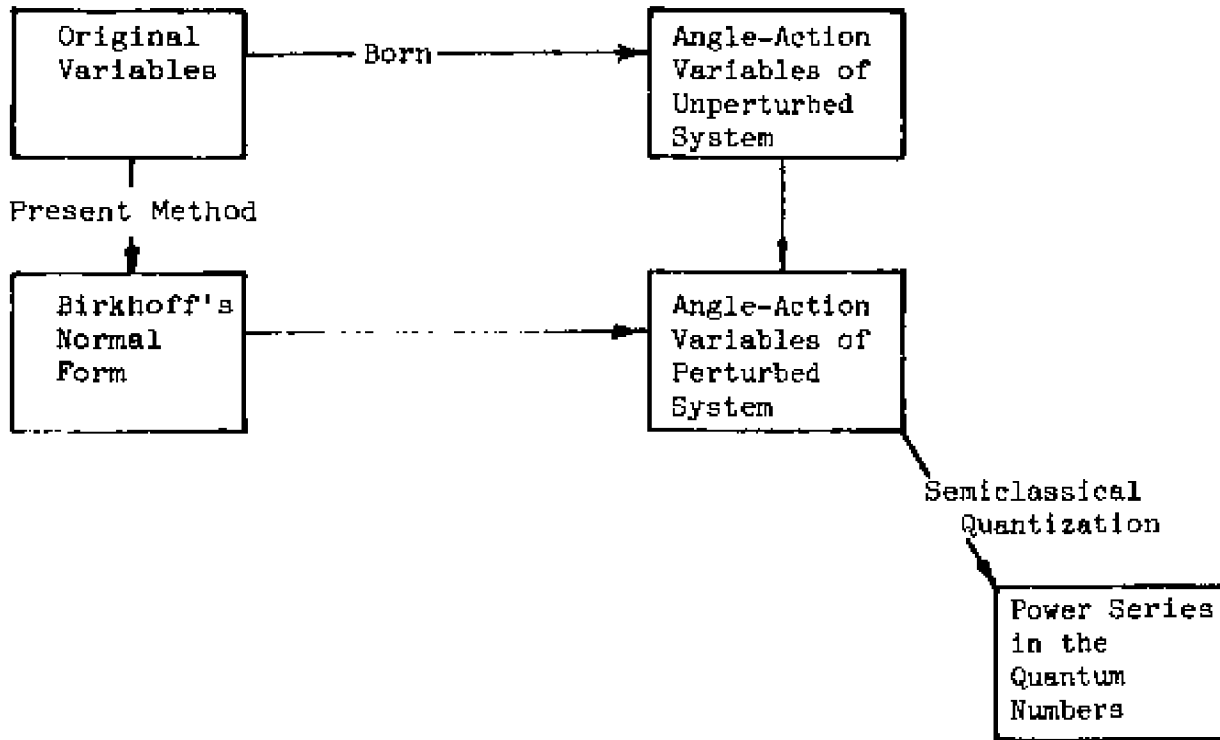


Fig. V.1. Schematic Comparison

order to obtain a power series in the quantum numbers. These steps are shown schematically in Fig. V.1. The individual steps in the succession of canonical transformations are quite different. Born calculates the generating function by expanding it in a Fourier series and solving for the coefficients. In practice the Fourier series terminates after a finite number of terms, and the coefficients can be found without truncation or approximation.

The principal difference between the methods is in the way the terms of the power series are collected. Born's method is a true perturbation method, and as such collects terms by powers of a small parameter. Our method involves a power series, but terms are collected by powers of the coordinates and momenta. If successive orders in the original Hamiltonian are not chosen to be of homogeneous degree in the coordinates and momenta, then the methods will certainly produce a final result which is summed differently (i.e. the power series in the quantum numbers will not agree between the two methods.) For the potentials we treated, both methods yield identical results in their first correction to the unperturbed result. Since Born only lists results through second order, it is not known if higher orders agree; Born's method is very tedious to derive to higher order and we have not carried it out any further than second degree (which he lists in his book²²).

As for a comparison with other calculational techniques, such as quantum mechanical perturbation theory, it should be borne in mind that one of the main motivations for carrying out the present work was to

produce an efficient means for applying the semiclassical method to non-separable systems analytically. As such, the method is one of many tools which a physicist has at his disposal, and is not intended to entirely replace any other methods.

It must be expected that in some cases the present method will produce more accurate answers for a given order approximation than quantum mechanical perturbation theory, but such cases are probably not predictable. As for a comparison of ease of calculation, it should be possible to program quantum mechanical perturbation methods in MACSYMA, but the non-commutative algebra required will cause calculations to be much less efficient; furthermore, at present many powerful computational resources are not readily available in MACSYMA if noncommutative algebra is required. It may also be pointed out that in general, semiclassical methods offer the best opportunity for a physicist to apply his classical intuition in order to "picture" what is going on. Such methods therefore complement the usual quantum mechanical methods.

Since the present method is both semiclassical, and perturbational in nature, it suffers from limitations imposed by both approximations. Therefore unlike most semiclassical methods, it is expected that it will produce progressively less accurate results as the quantum numbers grow; it should produce the best results at low quantum numbers because the unperturbed limit is a harmonic oscillator, and the harmonic oscillator happens to be exactly solvable using semiclassical methods.

C. Extensions and Limitations

The extension of these quantization methods to more than two degrees should be straightforward. The procedure for the incommensurable case will be unchanged. As for the commensurable case, it is believed that if there is only one independent commensurability condition on the frequencies of the unperturbed harmonic oscillators, the normal form should be reduceable to a form which is cyclic in all but one canonical coordinate. If that can be done, then the final quantum condition can be supplied by treating the problem as a one-dimensional case, and numerically integrating and quantizing a phase integral, as was done in the commensurable case treated here.

If there is more than one independent commensurability condition (say there are s such conditions, where s is less than the number of degrees of freedom f) then it is believed that the normal form can be reduced to a form which is cyclic in all but s canonical coordinates. This form would correspond to a nonseparable system of s degrees of freedom. Although in this way a set of $(f-s)$ action variables could be quantized analytically, and the dimensionality of the problem would be reduced, it is not clear that the spectrum of the residual Hamiltonian could be calculated easily. If it were to show quasiperiodic motion, then the remaining s action variables could be calculated and quantized by, for example, the methods of Noid and Marcus, but Ford^{17b,c} has found cases in which systems with two independent commensurability conditions appear to display predominantly ergodic behavior at all energies.

A practical consideration in the generation of the Birkhoff normal form is the number of terms which a Hamiltonian will contain. Higher degree terms generated while transforming lower degree terms into normal form will be numerous. In general, the part of the Hamiltonian of degree m , which has not yet been placed in normal form, will contain up to

$$\frac{(f + m - 1)!}{(f - 1)! m!} \quad (V.1)$$

individual terms (where f = total number of coordinates and momenta). In the case which we treated (two degrees of freedom, terms through degree 8) intermediate forms of the Hamiltonian require that almost five hundred terms be handled. If the calculation is done using MACSYMA, then storage capacity for three five-hundred term polynomials must be available (that is, for the original Hamiltonian, the final Hamiltonian and the generating function). Treating three degrees of freedom would generate six times as many terms as did two degrees of freedom. If the calculation is done using extended precision for the numerical coefficients, then correspondingly more core space must be available. We found that single precision calculations would fit in the available core space, but that when extended precision calculations were made, core storage capacity was exceeded, requiring that intermediate results be written onto disk storage. While this did not increase the required CPU time, it did increase elapsed time for a calculation by a factor of three. Presently special LISP machines are

being developed which will have a substantially increased storage capacity (the primary limitation here is the number of address bits available in the current implementation of MACSYMA).

A further consideration which must be discussed is the rate of convergence of the Birkhoff normal form. As discussed in Chap. IV, the Birkhoff normal form is known to diverge in general. Nevertheless, as this work and the work of Gustavson has shown, the normal form sometimes possesses a sort of false convergence such that if it is truncated, it can accurately characterize a system. Beyond this, however, we must determine whether the false convergence will be fast enough to make the series useful. The cases which we have discussed so far have displayed a sufficiently fast convergence, but we have found cases in which convergence was not rapid. For example, if the parameters for eqn. (III.5) are chosen

as

$$\begin{aligned} \omega_1 &= 0.7 & \lambda &= -0.1 \\ \omega_2 &= 1.3 & \eta &= 0.1 \end{aligned}$$

it is found that the coefficients of every order through degree eight terms in the normal form are of order unity. (Note that this corresponds to simply interchanging the values of frequency for the incommensurable case treated earlier.)

D. Applications

The first area which suggests itself is certainly the study of vibrational spectra of polyatomic molecules. No rotational effects have

been included here, but these effects have been studied extensively by others and methods for including them have been developed. It should be possible to include such effects in our calculations.

Our method might also find application in the study of vibrational effects superimposed on electronic transitions. In both this, and the pure vibration case, the method could be used either to calculate energy levels from known potential surfaces, or to help fit potential surfaces to experimentally known spectra - the inversion problem.

Other applications also exist. For example, the present method should be applicable to a semiclassical calculation of vibrational effects in deformed nuclei. It may also have application to photodissociation and non-resonant absorption.

Finally, another significant aspect of this research is that it has provided an illustration of the usefulness of analytical computer methods such as MACSYMA. Such analytical computer methods can complement numerical computer methods. Like all computer methods, these are most easily adapted to performing straightforward but tedious jobs (such as performing canonical transformations on Hamiltonians which contain several hundred terms using generating functions which contain several hundred terms.) Advantages are that results may be calculated faster, and that there are fewer opportunities for error. Beyond such applications, the interactive mode of operation provides an opportunity of great potential.

Appendix I. REVIEW OF HAMILTON-JACOBI THEORY

In this appendix we begin by reviewing the basic goal of Hamilton-Jacobi theory - namely to find a transformation to new variables in which Hamilton's equations are easier to solve. To illustrate the method, the time-independent H-J equation is solved for the separable case. Finally action-angle variables are defined, and their properties are discussed.

Let us begin with a problem expressed in coordinates q_1 and momenta p_1 . These variables satisfy Hamilton's equations of motion,

$$\dot{q}_i = \frac{\partial H(q,p)}{\partial p_i} \quad (\text{A1.1})$$

$$-\dot{p}_i = \frac{\partial H(q,p)}{\partial q_i} \quad (\text{A1.2})$$

where H is the Hamiltonian, and where (q,p) is a shorthand notation for $(q_1, \dots, q_n, p_1, \dots, p_n)$. We would like to perform a transformation to new variables (Q,P) in which Hamilton's equations of motion are easier to solve.

Let us look for transformation equations in terms of a generating function F^0 which links old and new coordinates. Let

$$F = F_2(q, P) \quad (\text{A1.3})$$

where (q,P) is a shorthand notation for $(q_1, \dots, q_n, P_1, \dots, P_n)$. The

transformation equations for such a generating function are

$$p_i = \frac{\partial F_2}{\partial q_i} \quad (\text{A1.4})$$

$$Q_i = \frac{\partial F_2}{\partial P_i} \quad (\text{A1.5})$$

$$K = H + \frac{\partial F_2}{\partial t} \quad (\text{A1.6})$$

where F_2 is unknown and K is the Hamiltonian expressed in the new coordinates and momenta. By substituting equations (A1.4) and (A1.5) into (A1.6) we can write a differential equation which, if solved, would provide F_2 .

$$K\left(\frac{\partial F_2}{\partial P}, P\right) \equiv H\left(q, \frac{\partial F_2}{\partial q}\right) + \frac{\partial F_2}{\partial t} \quad (\text{A1.7})$$

The transformation is not completely specified until we choose conditions which we want the final variables to satisfy. For example, if we require the final Hamiltonian K to be identically zero, then Hamilton's equations in the new variables

$$\begin{aligned} \dot{Q}_i &= 0 \\ \dot{P}_i &= 0 \end{aligned} \quad (\text{A1.8})$$

could be trivially solved

$$\begin{aligned} Q_1 &= \text{constant} \\ P_1 &= \text{constant} \end{aligned} \quad (\text{A1.9})$$

For this case, the equation for F_2 is the time dependent Hamilton-Jacobi equation

$$H\left(\delta, \frac{\partial F_2}{\partial \delta}\right) + \frac{\partial F_2}{\partial t} = 0 \quad . \quad (\text{A1.10})$$

Alternatively, we could require that the new Hamiltonian be cyclic in all new coordinates

$$K = K(P_1, \dots, P_n) \quad . \quad (\text{A1.11})$$

Then the equations of motion would become

$$\begin{aligned} \dot{Q}_i &= \frac{\partial K}{\partial P_i} = \nu_i(P_1, \dots, P_n) \\ \dot{P}_i &= 0 \end{aligned} \quad (\text{A1.12})$$

which possess the immediate solution

$$\begin{aligned} Q_i &= \nu_i t + \beta_i \quad \text{where } \beta_i = \text{constant} \\ P_i &= \text{constant} \end{aligned} \quad (\text{A1.13})$$

and

$$K \equiv \alpha_1 = \text{constant} \quad .$$

The equation for F_2 in this case is the time independent H-J equation

$$H\left(\delta, \frac{\partial F_2}{\partial \delta}\right) - \alpha_1 = 0 \quad . \quad (\text{A1.14})$$

Taking K to vanish, or taking K to be cyclic in the new coordinates, are only two possible conditions to apply to the new Hamiltonian in eqn. A1.7; many other choices are also possible. The equation which results from other choices is the equation for the generating function which will provide the necessary transformation equations.

The solution to the time independent H-J equation leads to the concept of action-angle variables, and subsequently to a more precise definition of quasiperiodic motion. If the Hamiltonian has no explicit time dependence then we may look for a generating function with no explicit time dependence

$$F_2 = W(q, P) \quad (A1.15)$$

The complete solution of A1.14 will contain n arbitrary constants of which one will be purely additive (because W enters only within derivatives). Therefore there will be $n-1$ nontrivial constants of integration which together with α_1 form n independent constants $\alpha_1, \dots, \alpha_n$. The new constant momenta can be chosen as any n independent functions of the n constants of integration. Now, suppose that the generating function W which solves the H-J equation is separable, i.e.:

$$W = \sum_i W_i(q_i; \alpha_1, \dots, \alpha_n) \quad (A1.16)$$

Therefore

$$P_i = \frac{\partial W_i(q_i; \alpha_1, \dots, \alpha_n)}{\partial q_i} \quad (A1.17)$$

Now it can be shown that if the H-J equation has a solution of this type, and if the motion is bounded, then the motion of each coordinate can only be a libration or a rotation.⁹ For the librations of such a separable system, q_k varies back and forth between two fixed limits and we may consider the function

$$J_i = \oint p_i dq_i \quad (\text{A1.18})$$

integrated over one cycle of q_1 , where the $q_j (j \neq 1)$ are either held constant, or if allowed to vary, then returned to their original values without having passed through a full cycle, i.e.

$$J_i = \oint \frac{\partial W_i(q_i; \alpha_1, \dots, \alpha_n)}{\partial q_i} dq_i \quad (\text{A1.19})$$

(Because W is assumed separable, it can be seen that $p_i dq_i$ is an exact differential. This ensures the path-independence of the integral.) The function J_i is called the action variable. Since the q_i dependence has been integrated out,

$$J_i = J_i(\alpha_1, \dots, \alpha_n) \quad (\text{A1.20})$$

Let us choose the action variables to be the new momenta. Therefore

$$W = W(q_1, \dots, q_n; J_1, \dots, J_n) \quad (\text{A1.21})$$

$$K = \alpha_1 = K(J_1, \dots, J_n) \quad (\text{A1.22})$$

The canonical coordinates conjugate to J_i are known as the angle variables w_i . They are furnished from the transformation eqn. (A1.5):

$$w_i = \frac{\partial W}{\partial J_i} \quad (\text{A1.23})$$

The equations of motion provide the form

$$\begin{aligned} \dot{w}_i &= \frac{\partial K}{\partial J_i} \\ &\equiv \nu_i(J_1, \dots, J_n) \end{aligned} \quad (\text{A1.24})$$

which has the immediate solution

$$w_i = \nu_i t + \beta_i \quad (\text{A1.25})$$

Let us find the change in w_i due to the passing of q_j through one cycle, with other coordinates either held fixed, or allowed to vary, but being brought back to their initial values without having passed through a full cycle.

$$\begin{aligned} \Delta^{(j)} w_i &= \oint \delta w_i \\ &= \oint \frac{\partial w_i}{\partial g_j} dg_j \quad \text{no sum} \\ &= \oint \frac{\partial^2 W}{\partial g_j \partial J_i} dg_j \\ &= \frac{\partial}{\partial J_i} \oint \frac{\partial W}{\partial g_j} dg_j \\ &= \frac{\partial}{\partial J_i} \oint p_j dg_j \\ &= \frac{\partial J_j}{\partial J_i} \\ &= \delta_{ji} \end{aligned} \quad (\text{A1.26})$$

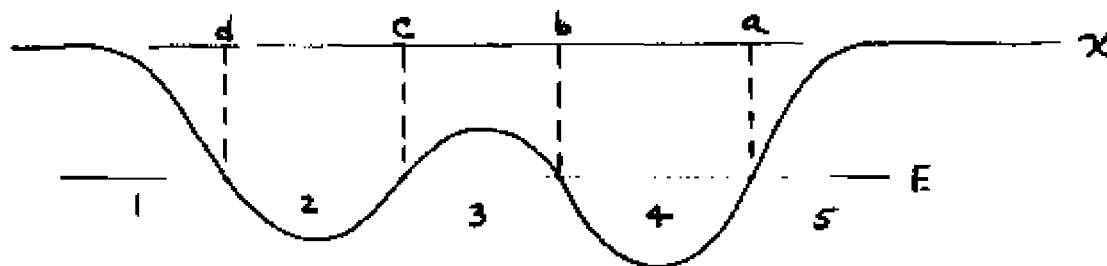
This shows that w_i will increase by unity if q_i passes through one cycle (with other coordinates restricted as above), but will be unchanged after q_j ($j \neq i$) passes through one cycle.

This example was for motion such that the coordinates vary between fixed limits (separable libration case). Similar results are found for motion such that the coordinates q_i increase monotonically, and the momenta p_i are periodic functions of the coordinates q_i (rotation case)⁹. The phase integral which provides J is integrated over one cycle of the motion (which will no longer be between fixed limits as in the libration case).

The above discussion was limited to the separable case. This illustrated important properties of angle-action variables, but serves only as a beginning for nonseparable cases. As is discussed in Chap. II, many of the concepts introduced here must be generalized in order to treat nonseparable systems.

Appendix II. ENERGY LEVELS FOR SYMMETRIC ONE-DIMENSIONAL
DOUBLE WELL

This appendix shows that the usual half-integral WKB quantization relation must be modified if there is more than one classically allowed region. Energy levels are calculated semiclassically for the symmetric one-dimensional double well shown in Fig. A2.1.



One-Dimensional Double Well

Fig. A2.1

We will make use of the connection relations shown in eqns. II.23 through II.26, the wavenumber k defined in eqn. II.19 for the allowed region, and $\kappa = ik$ in the forbidden region.

Boundary conditions require that the wavefunction in region 1 be a decreasing exponential

$$\psi_1 = \frac{1}{\sqrt{\kappa}} \exp\left(-\int_x^d \kappa dx\right) \quad (\text{A2.1})$$

Using the connection formula given in eqn. II.23 it follows that the wavefunction in region 2 is given by

$$\psi_2 = \frac{2}{\sqrt{k}} \cos \left(\int_d^x k dx - \frac{\pi}{4} \right) \quad (\text{A2.2})$$

Using the fact that

$$\int_d^x k dx = \int_d^c k dx - \int_x^c k dx \quad (\text{A2.3})$$

ψ_2 can be reexpressed in terms of an integral taken with reference to the turning point at c.

$$\begin{aligned} \psi_2 = & \frac{2}{\sqrt{k}} \sin \left(\int_d^c k dx \right) \cos \left(\int_x^c k dx - \frac{\pi}{4} \right) \\ & - \frac{2}{\sqrt{k}} \cos \left(\int_d^c k dx \right) \sin \left(\int_x^c k dx - \frac{\pi}{4} \right) \end{aligned} \quad (\text{A2.4})$$

We would now like to continue this solution into region 3. This requires that the connection formula given in eqn. II.25 be used in the wrong direction. We have warned that care must be taken if this is to be done. We know that the WKB method provides wavefunctions which are only approximations, in general. In this sense, we may say that the connection formulas can never be used backwards. On the other hand, boundary conditions require that eqn. A2.4 be exact within the WKB formalism. In particular, we have introduced no further approximations beyond those already

made in order to derive the WKB method (such as would occur for example, in round off error if along the way we had made floating point calculations on a computer). We will therefore use the connection formulas in the wrong direction; what we obtain we will simply call the WKB result.

Applying the connection formulas of eqns. II.25 and II.26 we obtain the wavefunction in region 3

$$\begin{aligned} \psi_3 = & \frac{1}{\sqrt{\kappa}} \sin\left(\int_d^c k dx\right) \exp\left(-\int_c^x \kappa dx\right) \\ & + \frac{2}{\sqrt{\kappa}} \cos\left(\int_d^c k dx\right) \exp\left(\int_c^x \kappa dx\right) \end{aligned} \quad (\text{A2.5})$$

Now, repeating the procedure from the opposite direction, we observe that boundary conditions require ψ_5 to be a decreasing exponential

$$\psi_5 = \frac{1}{\sqrt{\kappa}} \exp\left(-\int_a^x \kappa dx\right) \quad (\text{A2.6})$$

Applying the connection formula given in eqn. II.25 we obtain

$$\psi_4 = \frac{2}{\sqrt{k}} \cos\left(\int_x^a k dx - \frac{\pi}{4}\right) \quad (\text{A2.7})$$

Expressing this with respect to the turning point at b, we obtain

$$\begin{aligned} \psi_4 = & \frac{2}{\sqrt{k}} \sin\left(\int_b^a k dx\right) \cos\left(\int_b^x k dx - \frac{\pi}{4}\right) \\ & - \frac{2}{\sqrt{k}} \cos\left(\int_b^a k dx\right) \sin\left(\int_b^x k dx - \frac{\pi}{4}\right) \end{aligned} \quad (\text{A2.8})$$

Finally, we obtain a second expression for ψ_3 by applying eqn. II.23 (in the wrong direction) and II.24.

$$\begin{aligned} \psi_3 = & \frac{1}{\sqrt{\kappa}} \sin \left(\int_b^a k dx \right) \exp \left(- \int_x^b \kappa dx \right) \\ & + \frac{2}{\sqrt{\kappa}} \cos \left(\int_b^a k dx \right) \exp \left(\int_x^b \kappa dx \right) \end{aligned} \quad (\text{A2.9})$$

If eqns. A2.5 and A2.9 are to be consistent, then we must require that

$$2 \cos \left(\int_b^a k dx \right) = \sin \left(\int_d^c k dx \right) \exp \left(- \int_c^b \kappa dx \right) \quad (\text{A2.10})$$

and

$$\sin \left(\int_b^a k dx \right) = 2 \cos \left(\int_d^c k dx \right) \exp \left(\int_c^b \kappa dx \right) \quad (\text{A2.11})$$

For a symmetric potential, these conditions may be combined to yield

$$\tan \left(\int_{\substack{b \rightarrow a \\ d \rightarrow c}} k dx \right) = \pm 2 \exp \left(\int_c^b \kappa dx \right) \quad (\text{A2.12})$$

where the + sign is taken if k has the same sign in region 4 and region 2 (symmetric state), and the - sign is taken if k has opposite signs in region 4 and region 2 (antisymmetric state).

If the tunneling is small, we may expand eqn. A2.12 to obtain

$$\int_b^a k dx \simeq (n + \frac{1}{2})\pi \mp \frac{1}{2} \exp(-\int_c^b \kappa dx) \quad (\text{A2.13})$$

Thus we see that the usual half-integral quantization formula is modified even in the WKB formalism.

Appendix III. SEMICLASSICAL SOLUTION OF THE SCHRÖDINGER EQUATION

In this appendix we will investigate a method of constructing a uniform semiclassical solution to the multidimensional Schrödinger equation. This method was used by Ludwig²⁶ to construct approximate solutions to the Helmholtz equation and also by Khudyakov²⁷ for the case of variable index of refraction, and it is a generalization of a method by Langer²⁰ for treating one-dimensional systems.

If the WKB method is used to solve the Schrödinger equation, one obtains an asymptotic solution of the form

$$\psi \sim \sum_j A_j(x) e^{\frac{i}{\hbar} S_j(x)} \quad (\text{A3.1})$$

where the amplitude A_j varies slowly with x , the phase S_j is a solution to the H-J equation given by an action integral

$$S_j = \int p \cdot dx \quad (\text{A3.2})$$

($x \equiv (x_1, \dots, x_n)$, $P \equiv (P_1, \dots, P_n)$), and the sum includes contributions from a multiple valued solution to the H-J equation. This approximation breaks down at a caustic since the A_j go to infinity.

We treat here only the case of a single caustic having no folds or cusps and we assume we are not too close to the corners of the classically allowed region. Then of the four terms in (A3.1) we consider two

that represent waves propagating toward and away from the caustic as in Fig. A3.1:

$$A_- \exp \left[i \left(\frac{S_-}{\hbar} - \frac{\delta}{2} \right) \right] + A_+ \exp \left[i \left(\frac{S_+}{\hbar} + \frac{\delta}{2} \right) \right] \quad (\text{A3.3})$$

δ is the (yet unknown) phase change that results from passage through the caustic. Assuming A_{\pm} , S_{\pm} are given, we wish to obtain an approximation to ψ that remains regular at the caustic, and use this to determine δ .

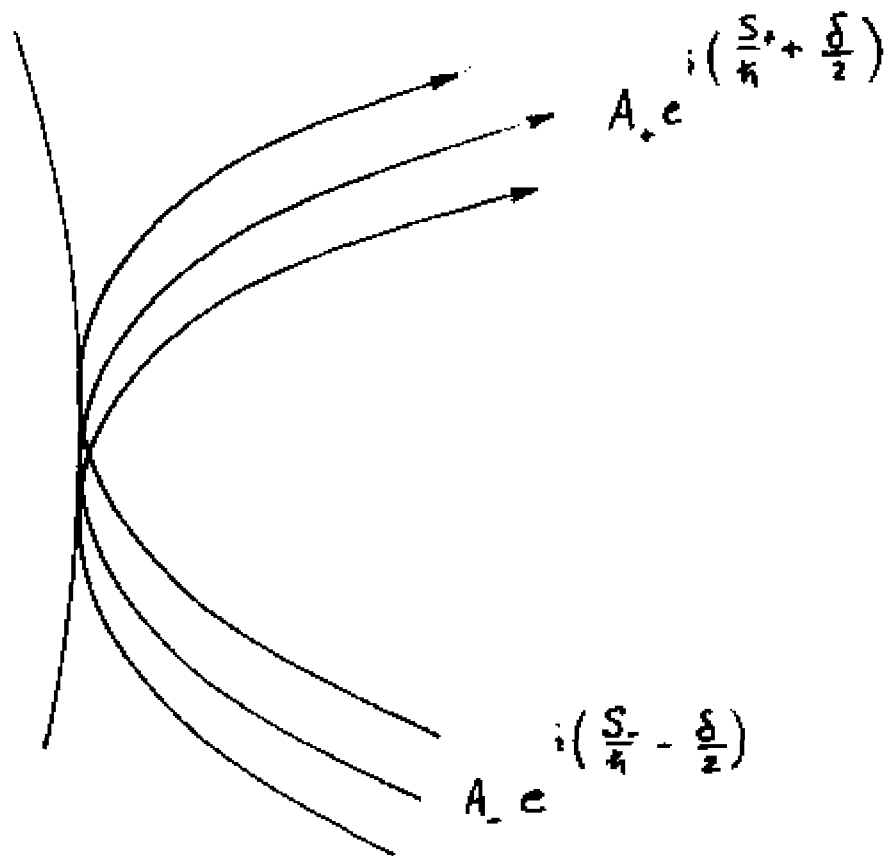


Fig. A3.1

Trajectories Turning at a Caustic

To accomplish this, Ludwig²⁶ proposes an ansatz of the form

$$\Psi(x) \sim \int \exp \left[\frac{i}{\hbar} \phi(x, \xi) \right] g(x, \xi) d\xi \quad (\text{A3.4})$$

with

$$\phi(x, \xi) = \theta(x) + p(x)\xi - \frac{1}{3}\xi^3 \quad (\text{A3.5})$$

where $\theta(x)$, $p(x)$ and $g(x)$, will be determined, and ξ is a single variable (not a vector).

Expanding $g(x, \xi)$ in a Taylor series

$$g(x, \xi) = g_0(x) + \xi g_1(x) + \dots \quad (\text{A3.6})$$

we obtain for Ψ the expansion

$$\Psi \sim e^{\frac{i}{\hbar}\theta(x)} \left\{ g_0(x) \int \exp \left[\frac{i}{\hbar} (p(x)\xi - \frac{1}{3}\xi^3) \right] d\xi + g_1(x) \int \xi \exp \left[\frac{i}{\hbar} (p(x)\xi - \frac{1}{3}\xi^3) \right] d\xi \right\} \quad (\text{A3.7})$$

Then noting the integral representation of the Airy function

$$V(t) \equiv \text{Ai}(-t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \exp \left[i \left(t\xi - \frac{1}{3}\xi^3 \right) \right] d\xi \quad (\text{A3.8})$$

we have

$$\psi(x) \sim 2\pi e^{\frac{i}{\hbar}\theta(x)} \left\{ \hbar^{1/3} g_0(x) V(\rho(x)/\hbar^{2/3}) - i\hbar^{2/3} g_1(x) V'(\rho(x)/\hbar^{2/3}) + \dots \right\} \quad (\text{A3.9})$$

Higher terms in this series contain successive powers of $\hbar^{1/3}$, and we will retain only the first two terms.

Before determining $\theta(x)$, $\rho(x)$, $g_0(x)$ and $g_1(x)$ let us examine the properties of (A3.9). For $\rho < 0$ the Airy function is decreasing, for $\rho > 0$ it is oscillatory and $\rho(x) = 0$ marks the transition between these two types of behavior. Accordingly, we must choose $\rho(x)$ such that the caustic, which is already determined from the classical trajectories, lies on $\rho(x) = 0$. The role of $\theta(x)$ is also clear: if a point is moved along the caustic the variation in phase of the wave function is given exclusively by $\theta(x)$.

The determination of the unknown functions θ , ρ , g_0 , g_1 involves the comparison of (A3.9) with (A3.3) and the verification that the resulting form actually satisfies the Schrödinger equation. Using the asymptotic form of the Airy function, which is obtained by applying the method of stationary phase to the integral form A3.8, we obtain directly

$$\psi \simeq \sqrt{2\pi\hbar} \left\{ \tilde{\rho}^{-1/4} (g_0 + \tilde{\rho}^{1/2} g_1) \exp i \left[(\theta + \frac{2}{3} \tilde{\rho}^{3/2})/\hbar - \pi/4 \right] + \tilde{\rho}^{-1/4} (g_0 - \tilde{\rho}^{1/2} g_1) \exp i \left[(\theta - \frac{2}{3} \tilde{\rho}^{3/2})/\hbar + \pi/4 \right] \right\} \quad (\text{A3.10})$$

PLEASE NOTE:

This page not included in
material received from the
Graduate School. Filmed
as received.

UNIVERSITY MICROFILMS

and to make this agree with (A3.3) we see that we should take

$$\begin{aligned}
 \theta &= \frac{1}{2} (S^+ + S^-) \\
 \frac{2}{3} p^{3/2} &= \frac{1}{2} (S^+ - S^-) \\
 g_0 &= \frac{1}{2} p^{3/2} (A_+ + A_-) \\
 g_1 &= \frac{1}{2} p^{3/2} (A_+ - A_-) .
 \end{aligned}
 \tag{A3.11}$$

Now although the right-hand-side of (A3.11) is defined only in the classically allowed region, near a simple caustic θ , p , g_0 and g_1 determined from (A3.11) can be smoothly continued into the forbidden region. This completes the determination of the unknowns in the ansatz.

It remains to show that the resulting function defined by (A3.9) and (A3.11) actually satisfies the Schrödinger equation,

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(x) \right] \psi(x) = E \psi(x)
 \tag{A3.12}$$

Substituting (A3.9) into (A3.12), collecting in powers of \hbar , and equating coefficients of different powers of \hbar separately to zero, the following equations result for θ and p :

$$(\nabla\theta)^2 + p (\nabla p)^2 - 2m (E - V) = 0
 \tag{A3.13a}$$

$$2 \nabla\theta \cdot \nabla p = 0
 \tag{A3.13b}$$

For g_0 and g_1 we obtain

$$2 \nabla \theta \cdot \nabla g_0 + g_0 \Delta \theta + 2 \rho \nabla \rho \cdot \nabla g_1 + \rho g_1 \Delta \rho + (\nabla \rho)^2 g_1 = 0 \quad (\text{A3.14a})$$

$$2 \nabla \rho \cdot \nabla g_0 + g_0 \Delta \rho + 2 \nabla \theta \cdot \nabla g_1 + g_1 \Delta \theta = 0 \quad (\text{A3.14b})$$

Equations A3.13 are equivalent to the eikonal equation as may be shown by multiplying the first by $\sqrt{\rho}$ and adding the second; thus

$$\nabla \left(\theta \pm \frac{2}{3} \rho^{3/2} \right) - 2m(E - V) = 0$$

which again identifies $\theta \pm \frac{2}{3} \rho^{3/2}$ with S_{\pm} . Similarly, from eqns. A3.14, we find that $\tilde{\rho}^{1/4} (g_0 \pm \tilde{\rho}^{1/2} g_1)$ obeys the same equation as A_{\pm} . This completes the proof that the ansatz approximately satisfies the Schrödinger equation.

Finally, again comparing (A3.10) with (A3.3) we find $\delta = -\frac{\pi}{2}$: passage through the caustic causes a "non-classical" phase loss of $\pi/2$.

Appendix IV. EXAMPLE FOR CALCULATION OF NORMAL FORM

This appendix provides an example of how the notation used in eqn. III.8c should be interpreted.

$$\Gamma^{(i)}(P, q) = H^{(i)}(P, q) + \sum \frac{1}{j!} \left[\left(\frac{\partial W^{(s)}}{\partial q} \right)^j \frac{\partial^{|j|} H^{(i)}}{\partial P^j} - \left(\frac{\partial W^{(s)}}{\partial P} \right)^j \frac{\partial^{|j|} \Gamma^{(i)}}{\partial q^j} \right] \quad i > s$$

$$\begin{aligned} l + |j| + |j|(s-1) &= i \\ 1 \leq |j| < l < i \\ l \geq 2 \quad s \geq 3 \end{aligned} \quad \text{(III.8c)}$$

This equation allows us to calculate the new higher degree terms of degree i which result due to the canonical transformation which converted terms of degree s into normal form. The equation employs an abbreviated notation for terms in a multidimensional Taylor expansion. The index j is a vector abbreviation with two elements for a two degree of freedom problem, i.e. $j = j_1, j_2$, the notation $|j|$ means $j_1 + j_2$, and $j!$ means $j_1! j_2!$. Terms in the sum are chosen subject to the constraints listed on i , s , and j .

As an example, consider the case when $s = 3$. This means that a canonical transformation has been used to transform third degree terms into normal form using the third degree generating function $W^{(3)}$. Now we must calculate higher degree terms ($i = 4, 5, 6, \dots$) which result.

In expanded notation, eqn. III.8c yields

$$\Gamma^{(4)}(P, g) = H^{(4)}(P, g) + \sum_{m=0}^1 \frac{\partial W^{(0)}}{\partial g_m} \frac{\partial H^{(4)}}{\partial P_m} + \sum_{\substack{m=0 \\ n=2-m}}^2 \frac{1}{m!n!} \left(\frac{\partial W^{(0)}}{\partial g_0} \right)^m \left(\frac{\partial W^{(3)}}{\partial g_1} \right)^n \frac{\partial^2 H^{(2)}}{\partial P_0^m \partial P_1^n}$$

- similar sums on Γ

$$\Gamma^{(5)}(P, g) = H^{(5)}(P, g) + \sum_{m=0}^1 \frac{\partial W^{(0)}}{\partial g_m} \frac{\partial H^{(5)}}{\partial P_m} + \sum_{\substack{m=0 \\ n=2-m}}^2 \frac{1}{m!n!} \left(\frac{\partial W^{(3)}}{\partial g_0} \right)^m \left(\frac{\partial W^{(3)}}{\partial g_1} \right)^n \frac{\partial^2 H^{(3)}}{\partial P_0^m \partial P_1^n}$$

- similar sums on Γ

$$\Gamma^{(6)}(P, g) = H^{(6)}(P, g) + \sum_{m=0}^1 \frac{\partial W^{(3)}}{\partial g_m} \frac{\partial H^{(6)}}{\partial P_m} + \sum_{\substack{m=0 \\ n=2-m}}^2 \frac{1}{m!n!} \left(\frac{\partial W^{(3)}}{\partial g_0} \right)^m \left(\frac{\partial W^{(3)}}{\partial g_1} \right)^n \frac{\partial^2 H^{(4)}}{\partial P_0^m \partial P_1^n} \\ + \sum_{\substack{m=0 \\ n=3-m}}^3 \frac{1}{m!n!} \left(\frac{\partial W^{(3)}}{\partial g_0} \right)^m \left(\frac{\partial W^{(3)}}{\partial g_1} \right)^n \frac{\partial^3 H^{(3)}}{\partial P_0^m \partial P_1^n}$$

- similar sums on Γ

Higher degree terms can be calculated, as desired.

Once this process is completed, all of the changes to higher terms resulting from the normalization of degree three terms have been found. After fourth degree terms have been normalized an analogous set of

equations (with appropriate modifications) gives the further modifications to the higher degree terms.

Gustavson tabulates the generating functions obtained for each degree for the H & H potential. These results may be used as a check of one's calculations if desired.

REFERENCES

1. a. W. Eastes and R. A. Marcus, *J. Chem. Phys.* 61, 4301 (1974)
b. D. W. Noid and R. A. Marcus, *J. Chem. Phys.* 62, 2119 (1975)
c. D. W. Noid and R. A. Marcus, *J. Chem. Phys.* 67, 559 (1977)
d. D. W. Noid, M. L. Koszykowski and R. A. Marcus, *J. Chem. Phys.* 67, 404 (1977)
e. D. W. Noid, M. L. Koszykowski, R. A. Marcus and J. D. McDonald, *Chem. Phys. Lett.* 51, 540 (1977)
f. D. W. Noid, private communication.
2. a. S. Chapman, B. C. Garrett and W. H. Miller, *J. Chem. Phys.* 64, 502 (1976)
b. W. H. Miller, *J. Chem. Phys.* 63, 996 (1975)
c. N. C. Handy, S. M. Colwell, W. H. Miller, *Discuss. Faraday Soc.* 62, 29 (1976).
3. M. C. Gutzwiller, *J. Math Phys.* 8, 1979 (1967); 10, 1004 (1969); 11, 1791 (1970); 12, 343 (1971); 18, 806 (1977).
4. a. I. C. Percival, *J. Phys.* A7, 794 (1974)
b. I. C. Percival, N. Pomphrey, *Mol. Phys.* 31, 87 (1976)
c. I. C. Percival, *J. Phys.* B6, L229 (1973)
d. I. C. Percival, preprint
e. N. Pomphrey, *J. Phys.* B7, 1909 (1974).

5. M. V. Berry and M. Tabor, Proc. Roy. Soc. (London) A349, 101 (1976).
6. a. K. S. Sorbie and N. C. Handy, Mol. Phys. 32, 1327 (1976)
 b. K. S. Sorbie, Mol. Phys. 32, 1577 (1976).
7. G. D. Birkhoff, Dynamical Systems, A.M.S. Colloquium Publications, New York, Vol. IX (1966).
8. F. G. Gustavson, Astron. J. 71, 670 (1966).
9. H. Goldstein, Classical Mechanics (Addison-Wesley Publishing Co., Inc., Reading, Mass., 1965).
10. a. J. Moser, SIAM Review 8, 145 (1966)
 b. J. Moser, Amer. Math. Soc. Memoirs 81, 1 (1968)
 c. J. Moser, Ann. Math. Studies 77 (Princeton Univ. Press. Princeton, N.J., 1973)
 d. J. Moser, Comm. Pure and Applied Math. IX, 673 (1956).
11. L. A. Pars, A Treatise on Analytical Dynamics (Heinemann Educational Books Ltd., London, 1965).
12. H. Poincaré, Les Méthodes Nouvelles de la Mécanique Céleste (Dover Publications, New York, 1957).
13. A. Wintner, Analytical Foundations of Celestial Mechanics (Princeton Univ. Press, Princeton, 1947) p. 96.
14. M. Hénon and C. Heiles, Astron. J. 69, 73 (1964).
15. A. N. Kolomogorov, Dokl. Akad. Nauk. SSSR 98, 527 (1954); Proc. International Congress of Mathematics, Noordhoff, Amsterdam, 1, 315 (1957).
16. V. I. Arnol'd, Izv. Akad. Nauk. SSSR Ser. Mat. 25, 21 (1961); Uspehi Mat. Nauk. 18, 81 (1963); Ibid., 18, 13 (1963).

17. a. J. Ford, *Fundamental Problems in Statistical Mechanics*, Vol. 3
(North Holland Publishing Co., Amsterdam, The Netherlands, 1975)
p. 215
- b. J. Ford and G. Lunsford, *Phys. Rev. A* 1, 59 (1970)
- c. G. Lunsford and J. Ford, *J. Math. Phys.* 13, 700 (1972).
18. A. Einstein, *Verhand. Deut. Phys. Ges.* 19, 82 (1917).
19. A. Messiah, *Quantum Mechanics* (John Wiley & Sons, Inc., New York, 1958) Ch. VI.
20. R. Langer, *Phys. Rev.* 51, 669 (1937).
21. J. B. Keller, *Ann. Phys.* 4, 180 (1958).
22. M. Born, *The Mechanics of the Atom* (Frederick Ungar Publishing Co., New York, 1960).
23. C. L. Siegel, *Ann. Math.* 42, 806 (1941)
- C. L. Siegel, *Math. Ann.* 128, 144 (1945)
- C. L. Siegel, *Vorlesungen über Himmelsmechanik*, Springer Verlag, 1957.
24. H. Rüssmann, *Math. Ann.* 137, 64 (1959).
25. MACSYMA Reference Manual (The Mathlab Group, Laboratory for Computer Science, MIT, 1977);[†]
Proceedings of the 1977 MACSYMA Users' Conference (NASA CP-2012).
26. D. Ludwig, *Comm. Pure and Applied Math* XIX, 215 (1966).
27. S. V. Khudyakov, *Soviet Physics JETP* 29, 507 (1969).

[†]The Mathlab group at the Laboratory for Computer Science, MIT is supported, in part, by the United States Energy Research and Development Administration under Contract Number E(11-1)-3070 and by the National Aeronautics and Space Administration under Grant NSG 1323.