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REGULAR AND IRREGULAR SPECTRA
OF MOLECULES

by

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ABSTRACT

A correspondence principle interpretation of the dynamics of classical non-separable Hamiltonian systems has led Percival (1973) to predict that for such systems there are two regions of the quantal energy spectrum with contrasting properties. Polyatomic molecules are described by non-separable Hamiltonians and with advancing experimental methods the relevance of Percival's predictions to molecular spectra is apparent. In this thesis eigenvalues for the Hénon-Heiles non-separable Hamiltonian are obtained using the full symmetry of the potential and it is shown that two regions of the quantal energy spectrum exist which behave differently under a slowly changing perturbation. Such behaviour is required by Percival for the existence of regular and irregular spectra.

This thesis also tackles the problem of determination of regular energy levels of polyatomic molecules. Semiclassical methods based on Einstein-Brillouin-Keller-Maslov (EBKM) quantization and a classical variational principle are described. They are applied to model potentials of up to two coordinates and promise to be effective for the determination from potential surfaces of large numbers of vibrational energy levels of suitable polyatomic molecules at energies intermediate between equilibrium and dissociation.

I N D E X

	<u>page</u>
INTRODUCTION	1
CHAPTER 1	
Section 1: Multiply periodic motions.	7
Section 2: Quantization rules.	9
CHAPTER 2	
Section 1: Dynamics of classical systems.	16
Section 2: Numerical experiment.	20
CHAPTER 3	
Section 1: Regular and irregular spectra.	31
Section 2: Relevance to Chemistry.	33
CHAPTER 4	
Section 1: Numerical test for regular and irregular spectra.	36
Section 2: Results.	40
Section 3: Conclusions.	53
CHAPTER 5	
Section 1: Introduction.	55
Section 2: Methods for multidimensional spectra.	55
Section 3: Assumptions of semiclassical method.	57

CHAPTER 6

Section 1:	Classical vibrations of a diatomic molecule.	60
Section 2:	Classical vibrations of a polyatomic molecule.	60

CHAPTER 7

Section 1:	Variational principles of Trkal and Van Vleck.	68
Section 2:	Percival's variational principle.	72

CHAPTER 8

Section 1:	Quantization.	77
Section 2:	Derivation of non-linear iteration equations.	78
Section 3:	A numerical iteration scheme.	80
Section 4:	An iteration scheme for energy functions.	82

CHAPTER 9

Section 1:	Analytic perturbation-variation methods.	85
Section 2:	Numerical perturbation-variation methods.	89
Section 3:	Numerical quantal methods.	89
Section 4:	Results.	91
Section 5:	Conclusions.	96

APPENDIX 1	100
------------	-----

APPENDIX 2	104
------------	-----

INTRODUCTION

For nearly fifty years wave mechanics has held a privileged position in Theoretical Physics. It has promised an understanding of results of experiments performed on atomic scales if only it is possible to proceed from the formulation of a given problem within the theory to its solution. Unfortunately it is often the case that solutions can only be found at considerable cost either of computer time or to the quality of solution: large matrix equations or many coupled wave equations have to be solved.

Recently much interest has been shown in the development of semiclassical methods which can be used as a substitute for wave mechanics. Most attention has been focused on collision processes of atoms and molecules [1], but this thesis will be concerned with bound states, especially of molecules. A philosophy similar to that adopted in "the old quantum theory" is followed whereby methods are sought which relate directly the classical and quantal solutions of a problem.

Chapter 1 of this thesis introduces the reader to some of the terminology of old quantum theory. The importance of multiply periodic solutions of Hamilton's equations of motion is stressed, action-angle variables are introduced, and a brief survey of quantization rules for the adiabatically invariant action variables is included. The chapter is not written as an historical review and it will be noticed that the vital work of Ehrenfest and his Adiabatic

Principle, and also Bohr's Correspondence Principle are not included. Excellent reviews already exist for these works [2].

Since the philosophy of the old quantum theory is to take classical mechanics as far as possible before applying the quantum restrictions, an understanding of the classical mechanics of Hamiltonian systems is clearly desirable. Chapter 2 reviews various aspects of the dynamics of Hamiltonian systems. Both separable and non-separable Hamiltonians are considered. In connection with non-separable systems, the important Kolmogorov-Arnol'd-Moser (KAM) theorem [3] is stated. Numerical evidence is sought to extend knowledge of the phase space structure of non-separable Hamiltonian systems and thereby complement the KAM theorem. In particular the numerical experiments performed by Hénon and Heiles [4] on a simple two-dimensional non-separable system are considered in some detail.

On the basis of the KAM theorem and the numerical experiments of Hénon and Heiles and others, Percival [5] has conjectured some interesting properties of quantized non-separable systems. Chapter 3 contains a statement of Percival's results. For non-separable systems Percival predicts there are two regions of the quantal spectrum with contrasting properties. At low energies the energy levels belong to a regular spectrum while at higher energies it is predicted that energy levels exist belonging to an irregular spectrum. The distinction between regular and irregular energy levels is expected to become evident when the sensitivity of the energy levels to a slowly changing perturbation is tested: energy levels belonging to an irregular

spectrum are expected to be more sensitive to a slowly changing perturbation than those of a regular spectrum.

Chapter 4 presents the results of a numerical experiment [6] which confirms that for the non-separable Hénon and Heiles Hamiltonian regular and irregular energy levels do exist in the sense of the above definition. Since polyatomic molecules are described by non-separable Hamiltonians the results presented in this chapter lend support to the prediction of Percival [5] that the vibrational energy spectrum of polyatomic molecules will show a regular progression which will terminate abruptly at a maximum energy below the dissociation limit.

The methods of old quantum theory can also be used to determine bound states of Hamiltonian systems and related properties. For diatomic molecules with separable Hamiltonians, semiclassical methods based on the Rydberg-Klein-Rees (RKR) method have been used for many years in relating experimental observations to potential energy curves. The history of successful attempts to obtain energy spectra of multi-dimensional non-separable systems using semiclassical methods is very short. Chapter 5 includes a description of the methods of Marcus et al [7] and also Miller et al [8]. (The work of the last author post-dates the work carried out for this thesis).

In this thesis a different approach for obtaining energy spectra of non-separable systems is preferred. The line of approach (due to Percival) and the assumptions made are outlined in chapter 5.

Relevant properties of the classical motion of diatomic molecules and of polyatomic molecules are described in chapter 6. Unlike chapter 1, the description is biased heavily towards the "invariant toroids" which

play an essential role in quantization. Chapter 7 contains a variational principle for invariant toroids which is analogous to the variational principle for the energy of bound quantal states. The work of Trkal [9] and especially Van Vleck [10] figure predominantly in this chapter.

In chapter 8 the EBKM quantization rule is related to invariant toroids. A non-linear equation for the invariant toroids is obtained from the variational principle of chapter 7 and iteration schemes are described both for the numerical solution and for the analytic solution of this equation. The numerical iteration scheme is fundamentally different from the analytic scheme in that the former scheme holds action integrals constant while allowing Fourier amplitudes of the motion to vary, and the latter scheme holds the amplitudes constant but allows the action integrals to vary. In both cases, the subsequent determination of energy levels is straightforward.

Chapter 9 illustrates by example the use of the methods of chapter 8 for obtaining analytic expressions for the energy levels of model one- and two-dimensional systems. The results are compared, where possible, with quantal perturbation theory. Exact semiclassical energy levels are also obtained by using the numerical scheme of chapter 8 and their values are compared with exact quantal energy levels obtained by standard matrix diagonalization. Finally, a comparison is also presented with some results of the alternative Marcus and Miller approaches.

Much of the work appearing in chapters 5 to 9 has already been published [11].

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CHAPTER 1

SECTION 1 : Multiply periodic motions .

Before the introduction of wave mechanics in 1925, the "Old Quantum Theory" was developed so that properties of the energy spectra of atomic systems could be investigated.

The foundations of the old quantum theory involve a number of postulates which incorporate the quantum ideas [1]; the existence of stationary states, and the relation for the exchange of energy between atoms and electromagnetic fields. The description of the motions within the stationary states was assumed to be governed (approximately) by the laws of classical mechanics, and therefore in particular by Hamilton's canonical equations of motion:

$$\frac{d}{dt} p_k = - \frac{\partial H}{\partial q_k} , \quad \frac{d}{dt} q_k = \frac{\partial H}{\partial p_k} \quad (k=1,2,\dots,N) \quad (1).$$

q_1, q_2, \dots, q_N are a set of generalised space coordinates which determine the positions of the particles and whose number, N , is the number of degrees of freedom of the system. p_1, p_2, \dots, p_N are the momenta conjugated to them. H is a function of the p 's and q 's whose functional form is characteristic of the system. H can be regarded as the total energy E .

When the form of the Hamiltonian function permits a solution to equations (1) of the form

$$q_k = \sum_{\tau_1, \tau_2, \dots, \tau_N}^{\infty} B_{\tau_1, \tau_2, \dots, \tau_N}^{(k)} \exp\{i 2\pi(\tau_1 \theta_1 + \tau_2 \theta_2 + \dots + \tau_N \theta_N)\} , \quad (2)$$

$= -\infty$

the system is termed multiply periodic. The quantities $\theta_1, \theta_2, \dots, \theta_U$ are called angle variables and each have a period 2π . Their conjugate quantities, denoted by I_1, I_2, \dots, I_U are called action variables and play an essential role in the quantum theory. The number U , of pairs of action-angle variables is called the "periodicity" of the motion.

A canonical transformation relates the positions and momenta of equations (1) to the action-angle variables:

$$(\underline{p}, \underline{q}) \xrightarrow{S} (\underline{I}, \underline{\theta}) \quad (3)$$

$$p_k = \frac{\partial}{\partial q_k} S(\underline{q}, \underline{I}) \quad , \quad \theta_k = \frac{\partial}{\partial I_k} S(\underline{q}, \underline{I})$$

The generator, S , of the canonical transformation (3) is a solution of the classical Hamilton-Jacobi equation

$$H(\underline{q}, \frac{\partial}{\partial \underline{q}} S) = E \quad (4)$$

The energy of the system regarded as a function of the new variables depends only on I_1, I_2, \dots, I_U . As a consequence of the canonical equations of motion (1), the action variables remain constant during the motion, while the angle variables vary uniformly with time:

$$\theta_k = \omega_k t + \delta_k \quad (k=1,2,\dots,U) \quad (5)$$

where

$$\omega_k = \frac{\partial}{\partial I_k} E \quad (6)$$

are U fundamental frequencies of the motion. It therefore follows that every coordinate q_k can be expressed as a function of the time by an expression of the form

$$q_k = \sum_{\tau_1, \tau_2, \dots, \tau_U}^{\infty} A_{\tau_1, \tau_2, \dots, \tau_U}^{(k)} \exp\{i2\pi(\tau_1\omega_1 + \tau_2\omega_2 + \dots + \tau_U\omega_U)t\} \quad (7)$$

So that the solution (7) is unique, it is necessary that there exist no non-trivial relation of the form

$$\sum_{k=1}^U \tau_k \omega_k = 0 \quad (8)$$

where $\tau_1, \tau_2, \dots, \tau_U$ are a series of integers. Such a relation is called a "resonance condition", and the value $\sum_{k=1}^U |\tau_k|$ is the "order" of the resonance.

Section 2 : QUANTIZATION RULES.

Multiply periodic systems for which it is possible to write particle displacements in the form (7) have their stationary states fixed by U "conditions of state" or "quantization rules", which can be written in the following way:

$$I_k = (v_k + \alpha_k/4) \hbar \quad (k=1, 2, \dots, U) \quad (9)$$

Here $2\pi\hbar$ is Planck's constant, ν_R is a positive integer, and α_R is a counting index whose value depends on the system under consideration. For molecules, $\alpha_R = 2$.

The existence of one or more linear relations of the form (8) does not limit the generality of equation (9). If a resonance condition exists it is always possible to find a canonical transformation which replaces the variables I, θ by linear combinations of these variables so that among the new variables no resonance conditions are satisfied.

Earliest forms of quantization rules make no mention of α_R . Sommerfeld [2] and Wilson [3] postulated that when the periodicity of the motion is equal to the number of degrees of freedom of the system ($U = N$), the stationary states are determined by the conditions

$$I_k = \nu_k \hbar \quad (k = 1, 2, \dots, N) \quad (10)$$

with the I_k 's identified with the phase integrals

$$\frac{1}{2\pi} \oint p_k dq_k = I_k \quad (11)$$

and the integral taken over are complete period of the q_k -motion. This seemed to fit well with Planck's important work concerning the selected states of a simple harmonic oscillator [4].

The Sommerfeld-Wilson conditions clearly depend on the choice of coordinates, and not every choice can give the correct quantization. Schwartzschild [5] and Epstein [6] proposed that the coordinates

should be chosen so that the action function S , which is a solution of the Hamilton-Jacobi equation, can be expressed as a sum over N separated action functions, each depending on a single coordinate only. Einstein [7] was unhappy about this proposal "The separation has nothing to do with the quantum problem" [7]. He was dissatisfied that the Schwartzschild-Epstein theory was not invariant under the canonical transformations of classical mechanics.

Einstein was able to write down quantization rules free from the above criticisms. His theory was based on the invariant differential sum

$$\sum_{k=1}^N p_k dq_k \quad (12)$$

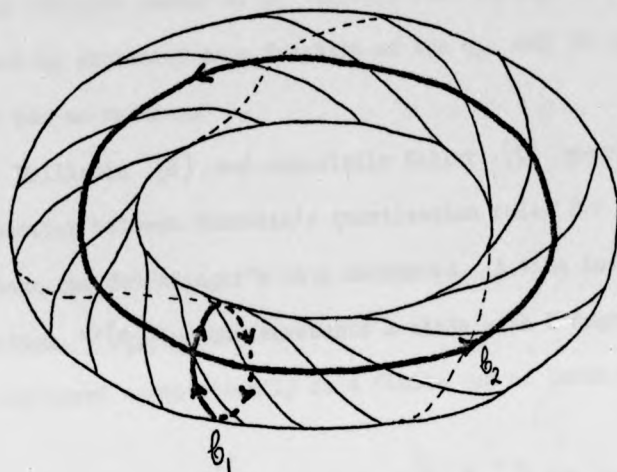
Einstein's quantization rules are given by invariant line integrals of the form

$$I_k = \frac{1}{2\pi i} \oint_{\mathcal{C}_k} \sum_{r=1}^N p_r dq_r = \nu_k \hbar \quad (13)$$

along closed curves \mathcal{C}_k in coordinate space which have no need to be classical trajectories. For separable systems these quantization rules reduce to the Schwartzschild-Epstein conditions.

In order to obtain N independent quantum conditions, the integrations of equations (13) have to be performed along N closed curves which cannot be deformed into one-another without crossing a singularity of the integrand. The N independent closed curves define as a direct product N -dimensional surfaces in the phase space which have the geometry of N -dimensional toroids. Figure 1 shows a sketch of a 2-dimensional toroid.

Figure 1



2-dimensional toroid showing independent closed curves b_1, b_2 used for quantization.

Einstein noted that the integrations in equation (13) require that through any element $d\tau$ in the q_r -space, only a finite number of momentum vectors p_r belong, for only then is it possible to express the p_r as one- or many-valued functions of the q_r . If an infinite number of p_r vectors pass through $d\tau$, p_r cannot be expressed as a function of the q_r and the quantization rule has no meaning.

Brillouin [8] and especially Keller [9] provided a connection between Einstein's quantization rules for non-separable systems and Schrodinger's wave mechanics. A time independent wave function $\Psi(q_r)$ which represents a state with N degrees of freedom is expressed asymptotically as a finite sum of terms of the form

$$\Psi(q_r) \underset{\hbar \rightarrow 0}{=} \sum_{k=1}^N A_k(q_r) \exp\{i\hbar^{-1} S_k(q_r)\} \quad (14)$$

A_k is a normalization factor and S_k is a classical action function of the coordinates. S_k is a solution of the classical Hamilton-Jacobi equation (4).

The requirement of quantum mechanics that $\Psi(q_r)$ be a single valued function of the q_r means that each S_k and the corresponding A_k must satisfy the conditions

$$\oint \nabla S_k \cdot ds_k = \frac{1}{2\pi} \oint \sum_{r=1}^N p_r dq_r = \hbar \left\{ \nu_k + \frac{i}{2\pi} \Delta \log A_k \right\} \quad (15)$$

where $\Delta \log A_k$ denotes the difference between any two values of $\log A_k$.

Analysis of the phase changes of A_k as the quantal waves are reflected from the caustics of the action functions shows

that the total change $\frac{i}{2\pi} \Delta \log A_k$ along a closed curve is given by

$$\frac{i}{2\pi} \Delta \log A_k = \alpha_k / 4 \quad (16)$$

where α_k is a register of the number of times a given classical trajectory encounters the caustics during one cycle of the motion. α_k is therefore a measure of the total phase change of the trajectory.

Equations (15) and (16) are together equivalent to the equation (9) which we write as

$$I_k = \frac{1}{2\pi} \oint_{C_k} \sum_{r=1}^N p_r dq_r = (J_k + \alpha_k / 4) \hbar \quad (k=1, 2, \dots, N) \quad (17)$$

Maslov [10] has recently provided a rigorous mathematical treatment of the quantization of general dynamical systems and has derived the condition (17) for Hamiltonian systems.

Equation (17) which defines the quantization of Hamiltonian systems with N degrees of freedom will be called the EBKM quantization rule.

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CHAPTER 2Section 1: Dynamics of classical systems.

The EBKM quantization rule can be used to obtain properties of a quantal energy spectrum in the semiclassical limit of high quantum numbers. In order to apply the quantization rule to a particular Hamiltonian system there must exist multiply periodic solutions to Hamilton's equations of motion for it is only for this class of solution that the EBKM condition has any meaning. Einstein indicated that for a non-separable Hamiltonian system it may be possible to find solutions to the equations of motion which are not multiply periodic; however he was unable to discuss which type of solution is expected to dominate in any given region of the phase space. A rigorous discussion of this problem was delayed until 1954 when A. N. Kolmogorov delivered an address [1] to the 7th International Congress of Mathematicians. To understand Kolmogorov's contribution it is useful to review some important aspects of the dynamics of Hamiltonian systems.

The motion of a bound separable system of N degrees of freedom consists of N independent one-dimensional motions and each such motion separately may be represented by a closed trajectory in a two-dimensional phase space. The separated motions are periodic with period T_{or} and angular frequency $\omega_{or} = 2\pi/T_{or}$; there is a constant of the motion, which may be chosen as an action variable I_{or} , and a canonically conjugate angle variable θ_{or} which varies from $-\pi$ to $+\pi$ in the course of one cycle of the motion.

The phase space of the whole system is $2N$ -dimensional. Any phase point χ in the phase space of the whole system is determined by values of all the action and angle variables. The point χ lies on an N -dimensional surface defined by keeping the action variables $I_{or}(\chi)$ fixed and allowing all the θ_{or} to vary. N independent closed curves on the surface are defined by fixing all θ_{or} except θ_{os} ($s = 1, 2, \dots, N$), and varying θ_{os} from $-\pi$ to $+\pi$. The curves so defined are independent in the sense that none of the curves may be transformed into any other by a continuous transformation which leaves it on the surface. The surface is an N -dimensional invariant toroid. The phase space of a separable system is almost everywhere filled with invariant toroids.

A trajectory which lies on a given toroid will approach arbitrarily close to any point on that toroid unless there exists some (non-trivial) resonance conditions of the form

$$\sum_{r=1}^N \tau_r \omega_{or} = 0 \quad (1)$$

where the τ_r are a set of integers. The system is said to be non-degenerate if no relation of the form (1) exists; otherwise it is degenerate or in resonance. If we have n relations (1), the number of independent frequencies is $N - n = U$ and the phase space trajectory lies in a region of only U dimensions. When there are $N - 1$ relations like (1) the system is completely degenerate. There remains only one angle variable θ and one frequency ω . The toroid consists entirely of closed trajectories.

Although relations of the form (1) seldom exist, arbitrarily close rational approximations to the ω_{or} result in resonances. In this case "quasi-periods" T_{os} can be found that satisfy relations

$$T_{os} = \tau_1 T_{o1} + \epsilon_1 = \tau_2 T_{o2} + \epsilon_2 = \dots = \tau_N T_{oN} + \epsilon_N \quad (2)$$

with errors $\epsilon_1, \epsilon_2, \dots, \epsilon_N$ as small as desired. If all the ϵ were zero for a certain choice of the τ_r , then T_{os} would be a common period and the system would be completely degenerate since equation (2) could be written as

$$\frac{\omega_{o1}}{\tau_1} = \frac{\omega_{o2}}{\tau_2} = \dots = \frac{\omega_{oN}}{\tau_N} = \omega_o = \frac{1}{T_{os}} \quad (3)$$

which represents $N - 1$ rational relations between the original frequencies ω_{or} . [2].

Suppose now that a small non-separable perturbation is applied to the separable system. Let the perturbed Hamiltonian H be written as

$$H = H^0 + b_1 H^1 \quad (4)$$

H^0 is the Hamiltonian function which describes the separable (unperturbed) system, while $b_1 H^1$ represents the non-separable perturbation. The independent motions are coupled together non-linearly and there is a possibility of large energy transfer between the unperturbed frequencies ω_{or} through internal resonance. This gives rise to the problem of "small divisors" in classical perturbation

theory and makes a study of the global dynamics of non-separable systems in terms of Hamilton-Jacobi theory impossible.

Kolmogorov [1] and later Arnol'd [3] and Moser [4] investigated the problem of what happens to the invariant surfaces of a separable system when a non-separable perturbation is switched on. Kolmogorov stated the following theorem, the proofs of which were later published by Arnol'd and by Moser.

KAM theorem

Let \mathcal{R} be a bounded $2N$ -dimensional region in the phase space of phase points $\mathcal{X} = (\underline{q}, \underline{p})$. If $H^0(\underline{q}, \underline{p})$ is a separable analytic Hamiltonian function in \mathcal{R} whose frequencies satisfy no low order resonance conditions, then for sufficiently small b_1 , invariant toroids

$$H(\underline{q}, \underline{p}) = H^0(\underline{q}, \underline{p}) + b_1 H^1(\underline{q}, \underline{p}) \quad (5)$$

fill most of \mathcal{R} .

The KAM theorem shows that if a bounded system is sufficiently close to being separable, then its phase space is almost everywhere dominated by the invariant surfaces required for EBKM quantization. However KAM says nothing about the nature of the residual regions. Neither does it say anything about systems that are far from being separable. It is necessary to appeal to numerical experiments in order to extend our knowledge of the phase space structure of non-separable systems. Such experiments provide an extrapolation from situations where current mathematical theorems can be applied to real physical systems.

Section 2 : numerical experiment.

Henon and Heiles [5] investigated a simple non-integrable Hamiltonian in connection with the question of the existence of a third integral of galactic motion. They were interested in the motion of a star in a galaxy whose gravitational potential has an axis of symmetry, taken to be the z -axis. The phase space of such a system is six-dimensional and there must therefore exist five independent conservative integrals of the motion; that is five independent functions which are constant along any trajectory. Two physically significant (isolating) integrals of the motion were known to exist, being the total energy and the angular momentum per unit mass of the star about the z -axis. In addition, two non-isolating integrals had been found. The problem was whether the remaining integral is isolating or non-isolating.

Henon and Heiles showed that the problem considered is equivalent to the motion of a particle of unit mass on a plane in an arbitrary non-separable potential $U(x, y)$. The potential function was chosen to have the form

$$U(x, y) = \frac{1}{2}(x^2 + y^2) + x^2y - \frac{1}{3}y^3 \quad (6)$$

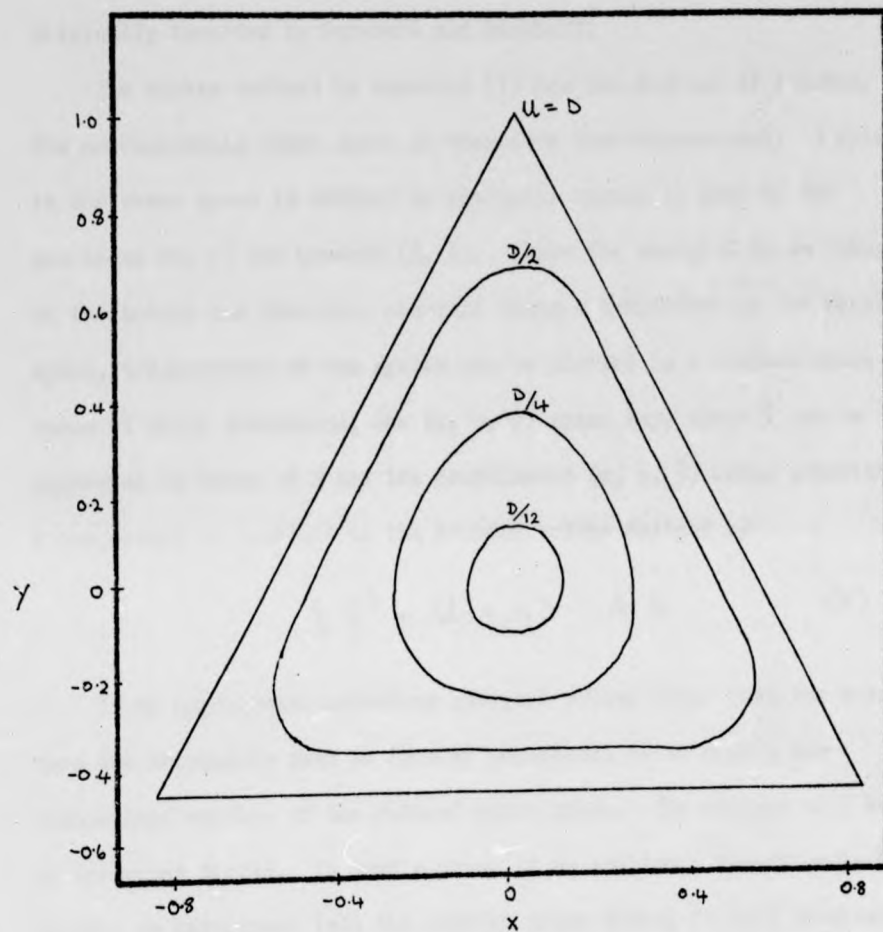
The equipotential lines for this potential are drawn in figure 1.

The phase space of the system has four dimensions (x, y, \dot{x}, \dot{y}) which means that there are three independent conservative integrals of the motion. The total energy of the system

$$E = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + U(x, y) \quad (7)$$

is an isolating integral, while a second integral can be shown to

Figure 1



Equipotential lines for

$$u(x,y) = \frac{1}{2}(x^2+y^2) + x^2y - \frac{1}{3}y^3.$$

$D = \text{ESCAPE ENERGY.}$

be non-isolating. To investigate the nature of the remaining third integral, Hénon and Heiles used the method of Surface-of-Section originally invented by Poincaré and Birkhoff.

The system defined by equation (7) has two degrees of freedom. The corresponding phase space is therefore four-dimensional. A point in the phase space is defined by assigning values to each of the positions (x, y) and momenta (\dot{x}, \dot{y}) . Since the energy E is an integral of the motion and therefore constant along a trajectory in the phase space, trajectories of the system can be plotted in a reduced phase space of three dimensions, the (x, y, \dot{y}) space say, since \dot{x} can be expressed in terms of E and the coordinates (x, y, \dot{y}) using equation (7). A trajectory is confined to the bounded volume defined by

$$\frac{1}{2} \dot{y}^2 + U(x, y) \leq E \quad (8)$$

If an independent isolating integral exists other than the energy then the trajectory must be further restricted to at most a two dimensional surface of the reduced phase space. The surface will be an invariant toroid. In such a case, if an arbitrary two-dimensional surface is introduced into the reduced phase space, it will intersect the toroid in a set of closed curves.

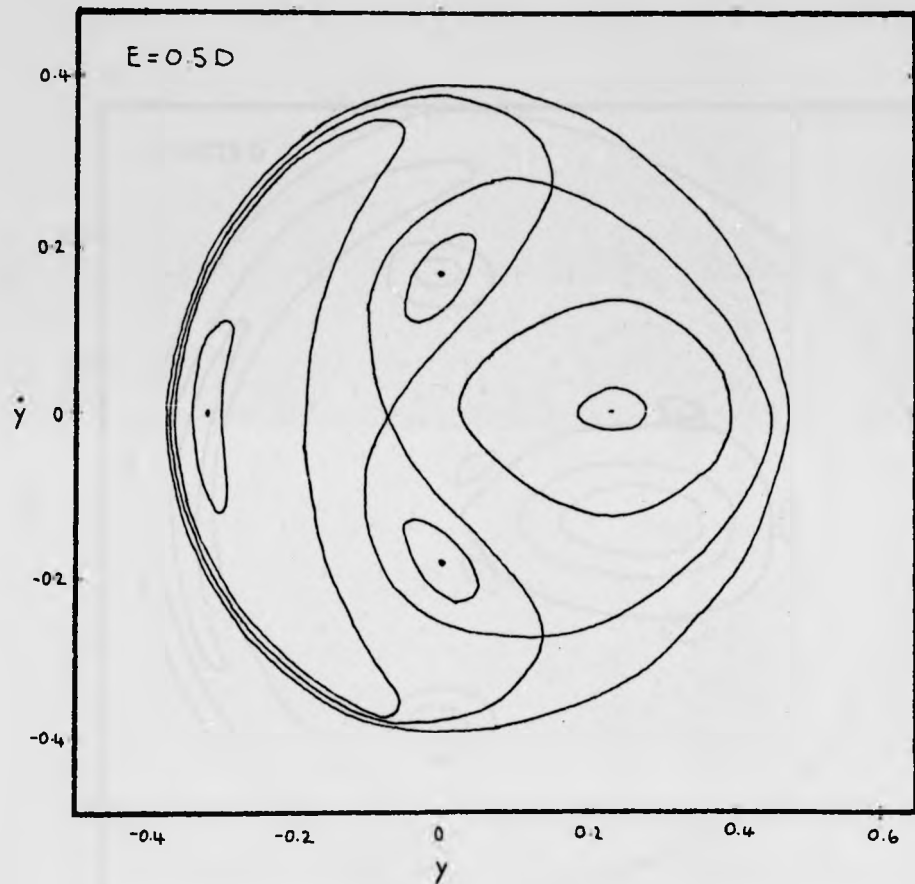
Hénon and Heiles considered the successive intersections of integrated trajectories with the plane $x = 0$ in the positive $-x$ direction, that is, the successive points which lie in the (y, \dot{y}) plane satisfying $x = 0, \dot{x} > 0$. If trajectories lie on two-dimensional surfaces then successive intersection points are expected to lie on level curves in the (y, \dot{y}) plane.

Figure 2 shows the results of Hénon and Heiles for a value of the energy equal to one half of the escape energy D , $E = 0.5D$. Here every trajectory investigated yielded a smooth curve of intersection points in the (y, \dot{y}) plane indicating the existence of a dense set of two-dimensional surfaces. For $E = 0.5D$ it seems that the Hénon and Heiles system is deep within the region of application of KAM.

Increasing the energy to $E = 0.75D$ the Hénon and Heiles system generated the mapping shown in figure 3. Although large areas of the allowed (y, \dot{y}) plane are still covered with level curves derived from trajectories lying on KAM surfaces, the remaining area is covered by a random looking splatter of points all of which were generated by one and the same trajectory. These points suggest that the trajectory fills a three-dimensional region of phase space, that is a region of the same dimension as the energy shell. Figure 4 shows what happens when the energy is increased still further. The dots shown in this figure are spread more or less uniformly over the allowed region of the (y, \dot{y}) plane, and were generated by a single trajectory. Every trajectory at $E = D$ yielded a similar pattern. Further experiment showed that if initially close starting conditions are chosen, the resulting trajectories diverge exponentially. This is a characteristic of stochastic behaviour.

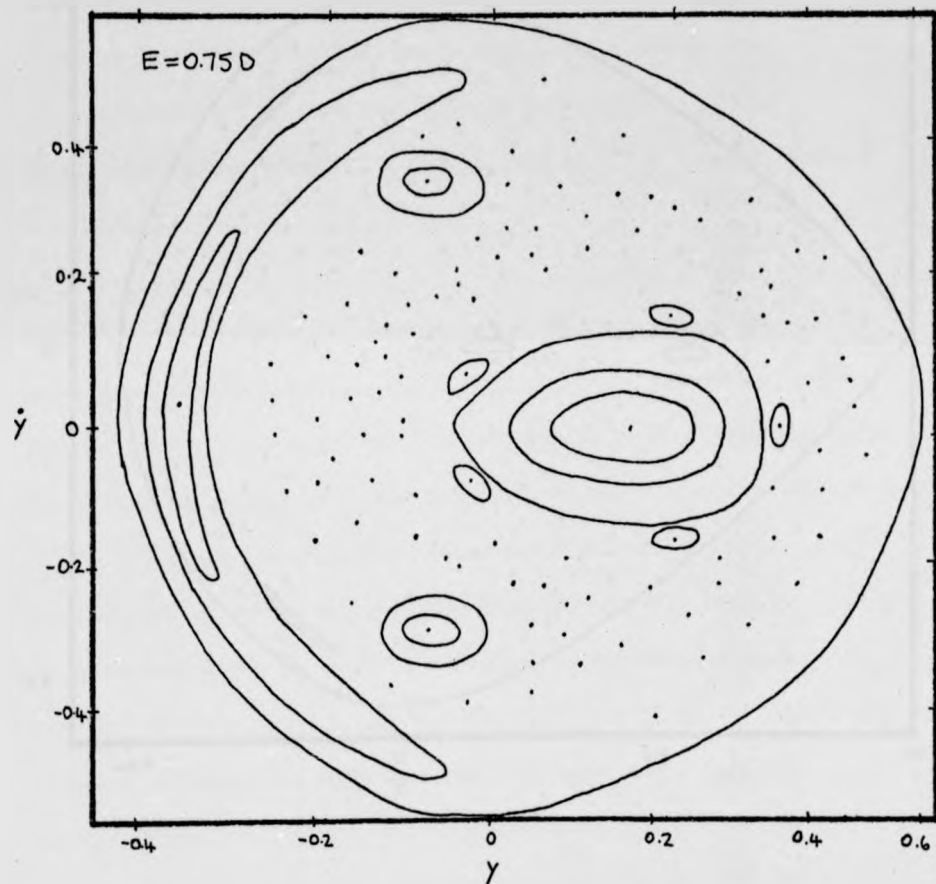
Percival [6] has named trajectories which lie on invariant surfaces regular trajectories and those which wander through the phase space irregular trajectories. Regions of phase space filled by surfaces are named regular regions while those regions which are devoid of surfaces are called irregular regions.

Figure 2



A surface of section cut in the phase space for the Hénon-Heiles system taken at an energy $E=0.5D$. The closed curves correspond to classical trajectories which lie on two-dimensional toroids.

Figure 3



Surface of section at $E=0.75D$ showing closed curves (as in figure 2) but also isolated points corresponding to a single trajectory.

Figure 4

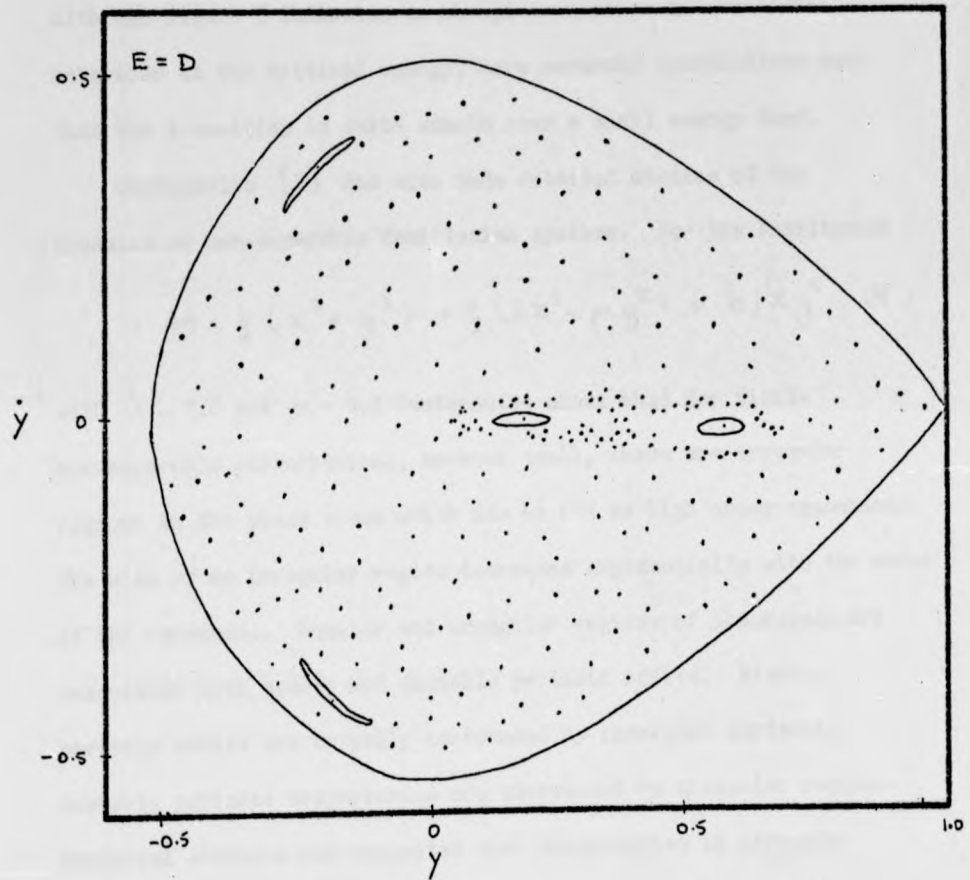
Surface of section at $E=D$

Figure 5 summarizes the results of Henon and Heiles. Up to a critical energy of $E^c \approx 0.68D$ the available phase space is filled almost entirely with invariant surfaces. For higher energies the volume filled by the surfaces (regular region) shrinks very rapidly. Although figure 5 indicates an abrupt transition to stochastic behaviour at the critical energy, more accurate calculations show that the transition is quite smooth over a small energy band.

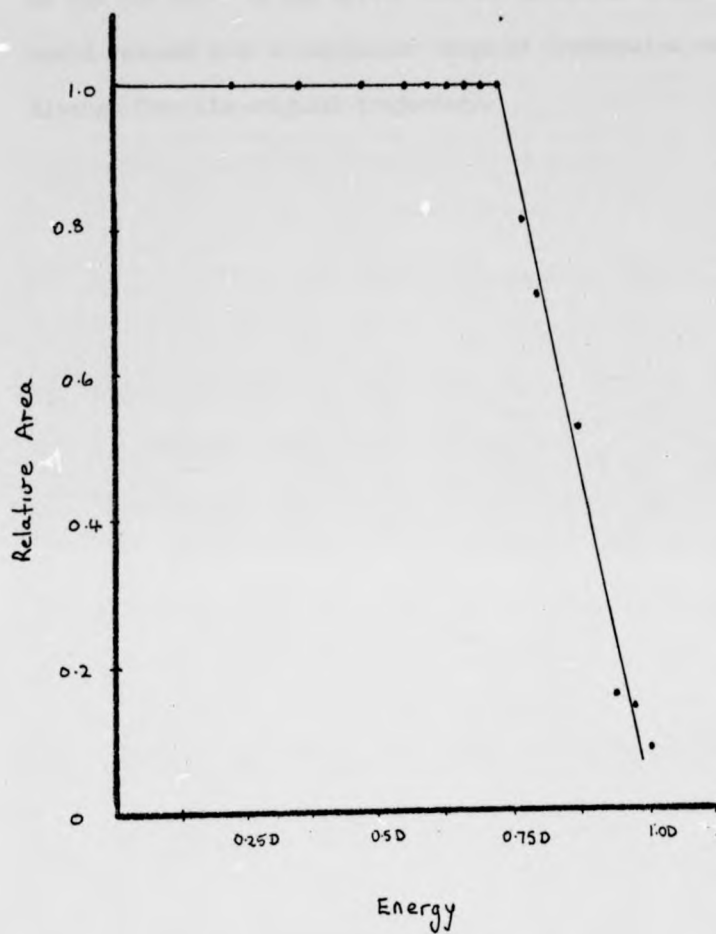
Contopoulos [7] has also made detailed studies of the dynamics of non-separable Hamiltonian systems. For the Hamiltonian

$$H = \frac{1}{2} (\dot{x}^2 + \dot{y}^2) + \frac{1}{2} (\lambda x^2 + \mu y^2) + b_1 x y^2 \quad (9)$$

with $\lambda = 1.6$ and $\mu = 0.9$ Contopoulos shows that for finite non-separable perturbations, however small, there are irregular regions in the phase space which may be due to high order resonances: The size of an irregular region decreases exponentially with the order of the resonance. Regular and irregular regions of phase space are associated with stable and unstable periodic orbits. Stable periodic orbits are normally surrounded by invariant surfaces; unstable periodic trajectories are surrounded by irregular regions. Numerical evidence has suggested that trajectories in irregular regions approach all points of a $(2N - 1)$ -dimensional region of phase space so that the frequency spectrum of a trajectory $(\underline{q}(t), \underline{p}(t))$ must be continuous.

On applying weak time-dependent perturbations to a system with a phase point in a regular region the system reponds at its resonant modal frequencies with decreasing effect as the order of the resonance increases. After a weak short-lived perturbation has ceased the

Figure 5



Relative area of Henon-Heiles surfaces of section covered by level curves as a function of energy.

new trajectory almost always stays on a toroid in the neighbourhood of the old one. If the system were an irregular trajectory, it would respond over a continuous range of frequencies and rapidly diverge from its original trajectory.

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CHAPTER 3Section 1 : Regular and Irregular spectra

Once a sound picture of the behaviour of classical non-separable Hamiltonian systems has been constructed, it is possible to obtain some properties of the corresponding quantal systems.

From the correspondence principle [1] and on the basis of the KAM theorem of classical mechanics and the numerical experiments of Hénon and Heiles, Contopoulos and others, Percival [2] was able to conjecture the following properties of quantized non-separable systems with N degrees of freedom (taken essentially straight from Percival's paper);

A high quantum level of the discrete energy spectrum of a bound quantal system belongs to either (R), a regular energy spectrum, or (I) an irregular energy spectrum. The regular energy spectrum and its associated states have the following properties:

(R1) A quantal state may be labelled by the vector quantum number

$$\underline{\nu} = (\nu_1, \nu_2, \dots, \nu_N) \quad (1)$$

(R2) A state with quantum number $\underline{\nu}$ corresponds to those phase space trajectories of the corresponding classical system which lie on an N -dimensional invariant toroid with action constants I_k given by the EBK quantum conditions

$$I_k = (\nu_k + \alpha_k/4) \hbar \quad (2)$$

(R3) The quantal state must resonate at frequencies close to those of the corresponding classical motion. Given two quantal states with

one ν_k differing by unity and all ^{others} the same, the Planck relation for their energy difference is

$$\Delta E_k = \hbar \omega_k \quad (3)$$

where ω_k is a fundamental frequency on the corresponding toroid.

(R4) A "neighbouring state" to a state ν^0 with energy E^0 is a state with quantum number ν close to ν^0 , with energy differences no more than a small multiple of the maximum $|\Delta E_k|$.

(R5) Under weak external perturbations the state ν^0 is much more strongly coupled to neighbouring states than to other states with the coupling tending to decrease rapidly with $|\nu - \nu^0|$.
 Not all states close in energy to a given state are neighbouring states, not even all those belonging to the same regular spectrum. However experiments which are able to select a few high ν -states of a regular spectrum have a high probability of selecting neighbouring states, so it is possible to observe the regularity Bound separable systems have a regular spectrum.

Properties of an irregular spectrum are predicted which are in striking contrast to those of a regular spectrum.

(I1) There is no unambiguous assignment of a vector quantum number to a state Ψ^0 .

(I2) The discrete bound state quantal spectrum must tend to a continuous classical spectrum in the classical limit. The energy differences

$$E(\Psi) - E(\Psi^0) = \hbar \omega \quad (4)$$

for fixed stationary state Ψ^0 and varying Ψ form a discrete distribution which tends to the continuous distribution in $\hbar\omega$. The distribution of levels of the irregular spectrum could take on the appearance of a random distribution.

(I3) There are no neighbouring 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 which correspond to the same irregular region of classical phase space. The number of such states is very large, of order ν_j^{N-1} where ν_j is a typical quantum number. The energies of the irregular spectrum are more sensitive to a slowly changing or fixed perturbation than those of the regular spectrum.

Section 2 : Relevance to chemistry.

Polyatomic molecules are examples of non-separable Hamiltonian systems. The predictions of Percival given above for general non-separable quantal systems are therefore also predictions of the behaviour of the energy spectra of polyatomic molecules when the relevant motions are coupled together non-linearly. The atomic motions which give rise to the pure vibrational spectrum of a polyatomic molecule is such an example. In the Born-Oppenheimer approximation, the vibrational energy spectrum of a polyatomic molecule is observed to be regular near equilibrium, except for Fermi

resonances which are a residual form of irregular spectrum. Near the dissociation limit the spectrum should be mainly irregular, with a large number of weak emission lines in place of a small number of strong ones. Percival predicts that a regular progression should be observed to terminate abruptly at a maximum energy below the dissociation limit.

What of the relevance to chemistry if such behaviour of energy spectra is found in real polyatomic (say triatomic) molecules? Theories of unimolecular reactions fall into two distinct types [3] which have varying amounts of success. There are Slater-type theories which assume that the vibrations of molecules are purely harmonic, and the statistical theories (for example the RRKM theory) which assume that the system phase points wander throughout the energy shell. If Percival's predictions are correct, it seems that a satisfactory theory of reactions may be developed with perhaps the critical energy appearing as an important parameter.

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CHAPTER 4SECTION 1: Numerical test for Regular and Irregular Spectra .

The predictions of Percival [1] regarding the proposed division of the quantal energy spectrum of non-separable Hamiltonian systems into two regions with contrasting properties - regular and irregular regions - clearly requires verification.

A straightforward test suggested by Percival is a test of the behaviour of the quantal energy levels of a non-separable Hamiltonian system under the influence of a fixed and of a slowly varying perturbation.

The simple non-separable Hamiltonian

$$H = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + \frac{1}{2}(x^2 + y^2) + U(x, y) \quad (1)$$

with

$$U(x, y) = b_1 \left(x^2 y - \frac{1}{3} y^3 \right) \quad (2)$$

and

$$b_1 = 1. \quad (3)$$

has become something of a test case in the literature of classical dynamics. The critical energy E^c at which value of the energy irregular regions of phase space become significant is well known

to be

$$E^c \approx 0.68 D \quad (4)$$

where

$$D = \frac{1}{6b_1^2} \quad (5)$$

is the depth of the potential well $U(x, y)$. Furthermore, Hamiltonian (1) possesses symmetry properties which can be used to good effect in any attempt to find its quantal energy spectrum. For these reasons, it is desirable to find eigenvalues of Hamiltonian (1) and to test their behaviour with respect to variations in the perturbation parameter b_1 .

The correspondence principle interpretation of the classical dynamics of the Hénon and Heiles Hamiltonian has been given by Percival [1]. It is expected that the quantal energy spectrum corresponding to Hamiltonian (1) will show a transition from a regular to an irregular spectrum at an energy given approximately by equation (4).

The equilateral symmetry of the Hénon and Heiles system becomes evident when the Hamiltonian (1) is expressed in polar coordinates:

$$H = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} r^2 + V(r, \theta) \quad (6)$$

where

$$V(r, \theta) = \frac{b_1}{3} r^3 \sin 3\theta \quad . \quad (7)$$

$V(r, \theta)$ is taken to be a (non-separable) perturbation on the basis Hamiltonian

$$H^0 = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} r^2 \quad (8)$$

which is the equation for a two-dimensional isotropic harmonic oscillator with unit frequency.

A more flexible choice for basis system is preferred however.

Writing

$$H^{0'} = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} \lambda r^2 \quad (9)$$

the full Hamiltonian (6) and (7) becomes

$$H = H^{0'} + \frac{b_1}{3} r^3 \sin 3\theta + \frac{1}{2} (1 - \lambda) r^2 \quad . \quad (10)$$

For computational purposes the pulsatace λ of the unperturbed system $H^{0'}$ was chosen to have that value which minimizes the volume of phase space required to represent the bound energy surfaces of the full Hamiltonian (10). A classical calculation yields for the optimum value of λ , $\lambda = \frac{1}{3}$ (see Appendix 1).

The basis wave functions whose linear combinations were taken to represent a wave function of the Hamiltonian H were of

the form

$$\phi_{\nu, l} = N_{\nu, |l|} F_{\nu, |l|}(r) \left(\exp\{il\theta\} \pm (-1)^l \exp\{-il\theta\} \right) \quad (11)$$

where

$$\nu = n_1 + n_2 \quad (12)$$

$$\text{and } l = n_1 - n_2 = \pm \nu, \pm(\nu-2), \dots, 0 \text{ or } \pm 1 \quad (13)$$

with n_1, n_2 integers > 0 .

The trigonometric functions (11) have a symmetry in common with the Hamiltonian, viz. invariance with respect to reflection in the y-axis.

Matrix elements of the perturbation

$$V'(r, \theta) = \frac{b_1}{3} r^3 \sin 3\theta + \frac{1}{2} (1-\lambda) r^2 \quad (14)$$

were obtained using the well-known "raising and lowering operator" technique [2] and are given below

$$\begin{aligned} \langle \nu, l | V'(r, \theta) | \nu, l \rangle &= \frac{1-\omega^2}{4\omega} (\nu+1) \\ \langle \nu, l | V'(r, \theta) | \nu+1, l \pm 3 \rangle &= \pm \frac{b_1}{4(2\omega)^{3/2}} [(\nu \mp l)(\nu \pm l + 2)(\nu \pm l + 4)]^{1/2} \\ \langle \nu, l | V'(r, \theta) | \nu-1, l \pm 3 \rangle &= \pm \frac{b_1}{4(2\omega)^{3/2}} [(\nu \mp l - 2)(\nu \mp l)(\nu \pm l + 2)]^{1/2} \quad (15) \\ \langle \nu, l | V'(r, \theta) | \nu \pm 2, l \rangle &= \frac{1-\omega^2}{8\omega} [(\nu \pm l + 1 \pm 1)(\nu - l + 1 \pm 1)]^{1/2} \\ \langle \nu, l | V'(r, \theta) | \nu \pm 3, l \pm 3 \rangle &= \pm \frac{b_1}{12(2\omega)^{3/2}} [(\nu \pm l + 6)(\nu \pm l + 4)(\nu \pm l + 2)]^{1/2} \\ \langle \nu, l | V'(r, \theta) | \nu-3, l \pm 3 \rangle &= \pm \frac{b_1}{12(2\omega)^{3/2}} [(\nu \mp l)(\nu \mp l - 2)(\nu \mp l - 4)]^{1/2} \end{aligned}$$

Only states with l quantum number differing by multiples of three are coupled by the perturbation. There is consequently a splitting of the Hamiltonian matrix into three submatrices according to whether the matrix elements (15) are derived from states of the unperturbed system with $l = 0, +1$ or -1 . Each submatrix is further split by the reflection symmetry possessed by the Hamiltonian: Only unperturbed states with different parity are coupled by the perturbation.

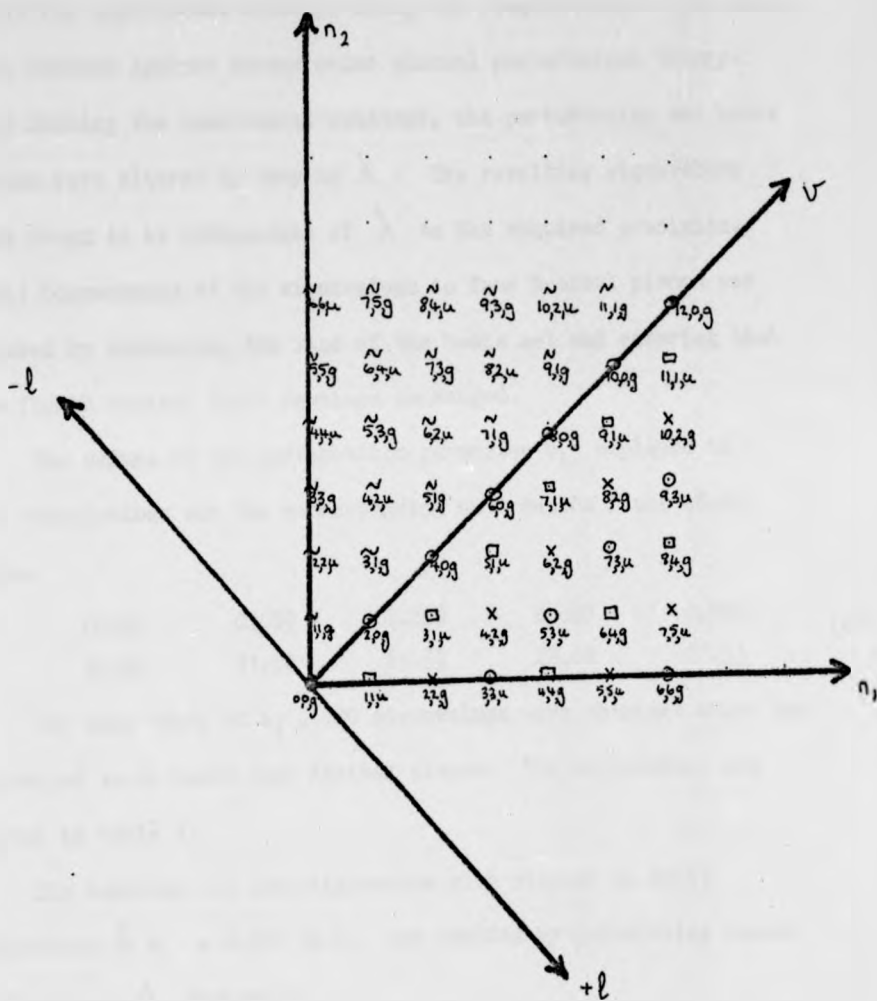
Figure 1 illustrates the coupling scheme for the Hénon and Heiles potential. Each unperturbed state has three labels; quantum numbers v and $|l|$, and the parity - g (*gerade*) for even (cosine) states or u (*ungerade*) for odd (sine) states. There are four independent groups of unperturbed states. Only states within a given group are coupled by the perturbation.

Section 2 : Results .

The quantal energy spectrum of the Hénon and Heiles system was obtained by separate diagonalization of each of four Hamiltonian submatrices. The matrices have to be truncated. The order was chosen large enough to ensure convergence to at least four decimal places for all those eigenvalues of interest. The problem of convergence is discussed later.

Five values of the perturbation parameter b_1 were chosen for the computations. For each value of b_1 matrices of order M ranging between 176 and 234 were diagonalized. The method of diagonalization employed the Householder technique for reducing the input matrix to tridiagonal form, followed by the Sturm Sequence method for

Figure 1.



Coupling scheme for matrix elements of Hénon-Heiles potential. EACH basis state is labelled by $v = n_1 + n_2$, $|l| = |n_1 - n_2|$, and parity = g or u. Basis states with the same symbol are coupled together by the potential.

locating the roots [3]. The calculations were performed on an IBM 370/155 computer using double precision arithmetic.

Three checks were performed on the eigenvalues:

- (i) With a small value of the perturbation parameter b_1 , the first few eigenvalues obtained using the diagonalization procedure were checked against second order quantal perturbation theory.
- (ii) Holding the Hamiltonian constant, the perturbation and basis system were altered by varying λ . The resulting eigenvalues were found to be independent of λ to the required precision.
- (iii) Convergence of the eigenvalues to four decimal places was checked by increasing the size of the basis set and ensuring that the fourth decimal digit remained unchanged.

The values of the perturbation parameter b_1 employed in the calculations and the corresponding well depths D are shown below

b_1	0.090	0.089	0.088	0.087	0.086	(6)
D	20.58	21.04	21.52	22.02	22.53	

For each value of b_1 , 140 eigenvalues were obtained which had converged to at least four decimal places. The eigenvalues are listed in table 1.

The behaviour of each eigenvalue with respect to small increments $\delta b_1 = 0.001$ in b_1 was studied by calculating second differences Δ defined by

$$\Delta_i = \left| [E_i(b_1 + \delta b_1) - E_i(b_1)] - [E_i(b_1) - E_i(b_1 - \delta b_1)] \right| \quad (17)$$

TABLE 1

EIGENVALUES OF THE HENON AND HEILES HAMILTONIAN

$$H = \frac{1}{2}(\dot{x}^2 + \dot{y}^2) + \frac{1}{2}(x^2 + y^2) + b_1(x^2y - \frac{1}{3}y^3)$$

<u>$b_1 = 0.090$</u>	<u>$b_1 = 0.089$</u>	<u>$b_1 = 0.088$</u>	<u>$b_1 = 0.087$</u>	<u>$b_1 = 0.086$</u>
0.9995	0.9995	0.9996	0.9996	0.9996
1.9982	1.9982	1.9983	1.9983	1.9983
2.9859	2.9862	2.9865	2.9868	2.9871
2.9954	2.9955	2.9956	2.9957	2.9958
3.9709	3.9716	3.9722	3.9728	3.9735
3.9905	3.9907	3.9909	3.9911	3.9913
3.9908	3.9911	3.9913	3.9915	3.9917
4.9502	4.9513	4.9524	4.9535	4.9545
4.9577	4.9587	4.9596	4.9605	4.9615
4.9925	4.9927	4.9929	4.9931	4.9932
5.9230	5.9247	5.9264	5.9281	5.9297
5.9234	5.9251	5.9268	5.9284	5.9301
5.9244	5.9261	5.9278	5.9294	5.9311
5.9966	5.9967	5.9969	5.9970	5.9971
6.8815	6.8841	6.8867	6.8893	6.8919
6.9108	6.9128	6.9149	6.9168	6.9188
6.9118	6.9139	6.9160	6.9180	6.9200
7.0025	7.0025	7.0026	7.0026	7.0027
7.0028	7.0028	7.0029	7.0029	7.0029

TABLE 1 Cont'd.

7.8294	7.8332	7.8369	7.8406	7.8442
7.8320	7.8357	7.8393	7.8429	7.8465
7.8555	7.8589	7.8622	7.8655	7.8687
7.8994	7.9018	7.9041	7.9064	7.9087
8.0112	8.0111	8.0110	8.0109	8.0108
8.7874	8.7923	8.7970	8.8017	8.8064
8.8051	8.8095	8.8138	8.8180	8.8222
8.8384	8.8427	8.8468	8.8509	8.8549
8.8876	8.8904	8.8931	8.8959	8.8985
8.8934	8.8958	8.8982	8.9006	8.9030
9.0215	9.0213	9.0211	9.0208	9.0205
9.7091	9.7155	9.7218	9.7281	9.7343
9.7215	9.7275	9.7334	9.7393	9.7450
9.7579	9.7638	9.7697	9.7754	9.7811
9.7760	9.7812	9.7863	9.7914	9.7964
9.8839	9.8868	9.8896	9.8923	9.8951
10.0336	10.0332	10.0328	10.0324	10.0319
10.0337	10.0333	10.0329	10.0324	10.0320
10.6646	10.6724	10.6801	10.6876	10.6951
10.6774	10.6846	10.6917	10.6987	10.7056
10.7102	10.7182	10.7259	10.7336	10.7411
10.7422	10.7486	10.7548	10.7609	10.7670
10.7812	10.7860	10.7908	10.7955	10.8002
10.8764	10.8797	10.8829	10.8861	10.8891
11.0478	11.0472	11.0466	11.0460	11.0454

TABLE 1 Cont'd.

11.5623	11.5719	11.5814	11.5908	11.6001
11.5918	11.6007	11.6095	11.6182	11.6267
11.6197	11.6296	11.6393	11.6488	11.6582
11.6263	11.6350	11.6436	11.6521	11.6604
11.7386	11.7444	11.7503	11.7560	11.7617
11.8692	11.8730	11.8767	11.8803	11.8838
11.8708	11.8744	11.8780	11.8815	11.8849
12.0635	12.0628	12.0620	12.0611	12.0603
12.5078	12.5196	12.5312	12.5426	12.5538
12.5251	12.5360	12.5467	12.5573	12.5676
12.5301	12.5427	12.5550	12.5671	12.5790
12.5652	12.5760	12.5865	12.5969	12.6070
12.6615	12.6691	12.6767	12.6842	12.6916
12.7070	12.7142	12.7212	12.7281	12.7349
12.8670	12.8710	12.8749	12.8787	12.8825
13.0806	13.0797	13.0787	13.0777	13.0767
13.0807	13.0798	13.0788	13.0778	13.0768
13.3877	13.4013	13.4147	13.4279	13.4409
13.4314	13.4450	13.4583	13.4713	13.4840
13.4331	13.4481	13.4628	13.4773	13.4915
13.4463	13.4596	13.4727	13.4856	13.4983
13.5835	13.5925	13.6015	13.6103	13.6190
13.6746	13.6832	13.6917	13.7001	13.0767
13.6857	13.6934	13.7009	13.7084	13.7158
13.8631	13.8677	13.8721	13.8764	13.8806

TABLE 1 Cont'd.

14.0993	14.0983	14.0971	14.0960	14.0947
14.3124	14.3293	14.3459	14.3622	14.3783
14.3164	14.3344	14.3520	14.3693	14.3862
14.3356	14.3522	14.3684	14.3842	14.3996
14.3545	14.3706	14.3865	14.4020	14.4173
14.5173	14.5284	14.5393	14.5502	14.5609
14.5186	14.5298	14.5408	14.5517	14.5624
14.6631	14.6718	14.6803	14.6887	14.6970
14.8581	14.8635	14.8687	14.8737	14.8784
14.8597	14.8650	14.8700	14.8748	14.8794
15.1189	15.1178	15.1166	15.1153	15.1140
15.1819	15.2005	15.2188	15.2368	15.2546
15.2055	15.2264	15.2469	15.2671	15.2868
15.2158	15.2369	15.2575	15.2775	15.2970
15.2267	15.2463	15.2656	15.2845	15.3029
15.4117	15.4246	15.4374	15.4499	15.4623
15.4518	15.4658	15.4795	15.4931	15.5063
15.4940	15.5050	15.5159	15.5267	15.5374
15.6370	15.6471	15.6570	15.6667	15.6762
15.8564	15.8625	15.8682	15.8737	15.8789
16.0695	16.0943	16.1181	16.1341	16.1340
16.0761	16.0994	16.1223	16.1448	16.1668
16.0919	16.1165	16.1404	16.1638	16.1866
16.1058	16.1276	16.1363	16.1355	16.1342
16.1402	16.1391	16.1383	16.1447	16.1665

TABLE 1 Cont'd.

16.1403	16.1401	16.1526	16.1739	16.1952
16.3111	16.3269	16.3424	16.3577	16.3728
16.3408	16.3565	16.3719	16.3871	16.4021
16.4466	16.4597	16.4726	16.4852	16.4977
16.6042	16.6166	16.6286	16.6402	16.6515
16.6170	16.6279	16.6387	16.6491	16.6594
16.8508	16.8584	16.8654	16.8719	16.8780
16.9355	16.9658	16.9953	17.0241	17.0523
16.9369	16.9623	16.9872	17.0117	17.0357
16.9381	16.9668	16.9949	17.0222	17.0490
16.9583	16.9858	17.0130	17.0395	17.0656
17.1597	17.1593	17.1584	17.1572	17.1557
17.2055	17.2249	17.2440	17.2628	17.2814
17.2116	17.2291	17.2466	17.2640	17.2811
17.2960	17.3112	17.3262	17.3409	17.3555
17.3904	17.4063	17.4219	17.4371	17.4521
17.5915	17.6043	17.6167	17.6287	17.6403
17.7678	17.8021	17.8334	17.8580	17.8726
17.7901	17.8241	17.8573	17.8898	17.9215
17.7923	17.8246	17.8560	17.8867	17.9166
17.8089	17.8367	17.8558	17.8669	17.8752
17.8509	17.8633	17.8829	17.9095	17.9376
17.8536	17.8629	17.8735	17.8893	17.9138
18.0771	18.0984	18.1193	18.1396	18.1591
18.1205	18.1423	18.1637	18.1849	18.2058

TABLE 1 Cont'd.

18.1834	18.1827	18.1818	18.1808	18.1802
18.2143	18.2330	18.2513	18.2691	18.2866
18.3191	18.3394	18.3590	18.3780	18.3965
18.3741	18.3893	18.4042	18.4188	18.4332
18.5550	18.5728	18.5888	18.6036	18.6175
18.5994	18.6406	18.6806	18.7195	18.7575
18.6115	18.6523	18.6916	18.7297	18.7665
18.6391	18.6744	18.7087	18.7422	18.7748
18.6413	18.6765	18.7122	18.7476	18.7825
18.8406	18.8509	18.8605	18.8694	18.8776
18.9420	18.9665	18.9908	19.0147	19.0384
18.9739	18.9974	19.0207	19.0439	19.0668
19.0612	19.0844	19.1067	19.1283	19.1491
19.1177	19.1412	19.1640	19.1861	19.2075
19.2019	19.2022	19.2092	19.2012	19.2001
19.2050	19.2049	19.2043	19.2035	19.2024
19.3170	19.3372	19.3560	19.3739	19.3911
19.3892	19.4381	19.4843	19.5270	19.5645
19.4343	19.4787	19.5228	19.5660	19.6082
19.4436	19.4888	19.5327	19.5751	19.616(3)
19.454(2)	19.4949	19.5313	19.5609	19.583(7)

where i denotes the particular eigenvalue under investigation.

Δ_i is a measure of the "smoothness" of response of the eigenvalue E_i to the change δb_1 in the perturbation. For the particular case of the Hénon and Heiles system, quantal perturbation theory yields

$$\Delta_i = \mathcal{O}(\delta b_1^4) \quad (18)$$

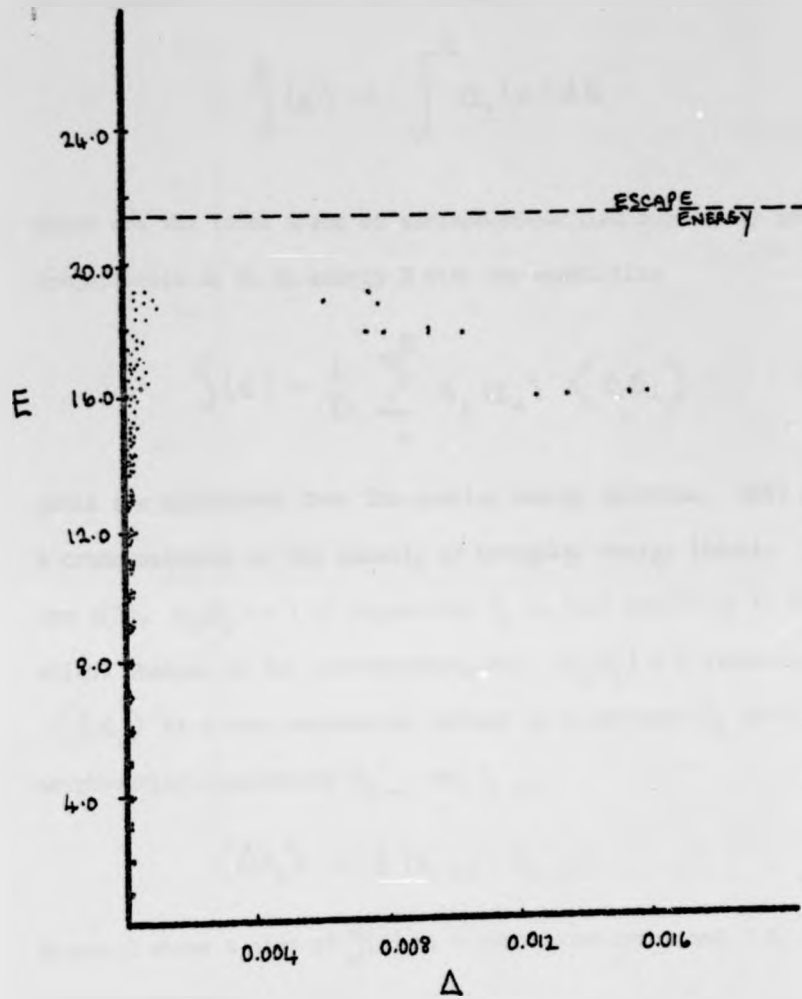
The values Δ_i for the Hénon and Heiles system are shown as a function of the energy E_i in figure 2. For energy levels E_i with energy less than $E = 16.0 \approx 0.74D$ all second differences Δ_i are very small (since the energy levels are computed to four decimal places the accuracy of the second differences, due to rounding errors, is ± 0.0002). For energy levels with energy greater than $E = 16.0$ however, eigenvalues are found with corresponding Δ_i values very much larger. These eigenvalues are evidently very sensitive to small changes in the perturbation. High order terms in the perturbation expansion become important for these eigenvalues.

Thus two types of eigenvalue are distinguished by their behaviour under a slowly changing perturbation.

Hénon and Heiles have plotted energy against relative area of surface-of-section covered by unstable trajectories (Chapter 2, figure 5). From their results the relative area a_I covered by unstable trajectories is given approximately as a function of the energy E by

$$\begin{aligned} a_I(E) &= 0 & E < 0.68D \\ &= 3.125 \left(\frac{E}{D}\right) - 2.125 & E > 0.68D \end{aligned} \quad (19)$$

Figure 2



The second differences Δ as a function of the energy E .

Each dot on the graph represents an eigenvalue of the Hénon and Heiles hamiltonian.

It is possible to compare the integrals

$$g(E) = \int^E a_I(E) dE \quad (20)$$

which are the total areas of surface-of-section covered by unstable trajectories up to an energy E with the quantities

$$S(E) = \frac{1}{D} \sum_i^E \rho_I(E_i) \langle \Delta E_i \rangle \quad (21)$$

which are calculated from the quantal energy spectrum. $S(E)$ represents a crude estimate of the density of irregular energy levels. In the sum $S(E)$, $\rho_I(E_i) = 1$ if eigenvalue E_i is very sensitive to the slight changes in the perturbation, and $\rho_I(E_i) = 0$ otherwise.

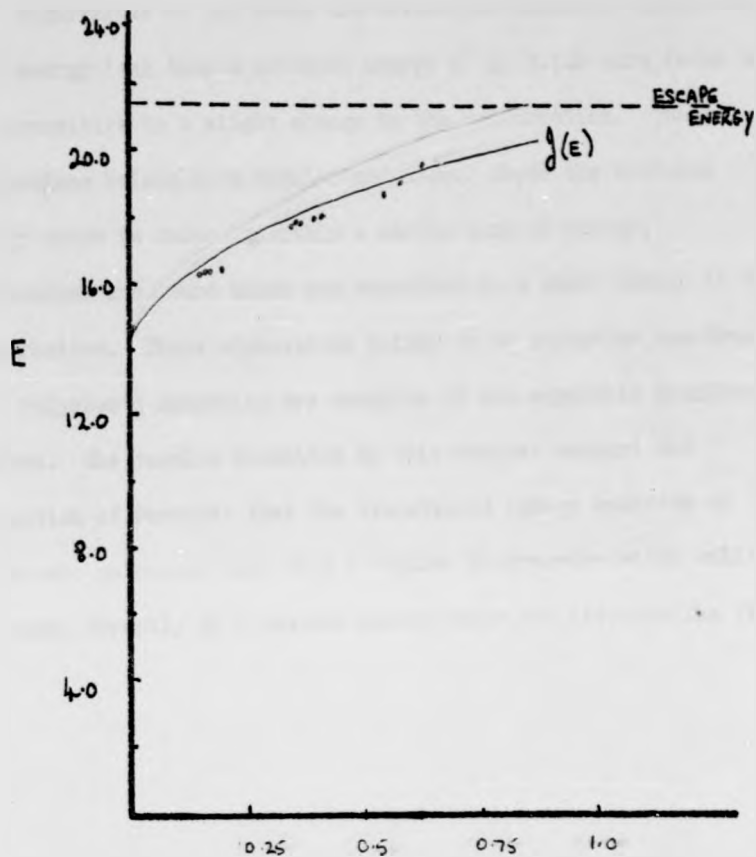
$\langle \Delta E_i \rangle$ is a mean separation between an eigenvalue E_i and its two neighbouring eigenvalues E_{i-1} and E_{i+1} .

$$\langle \Delta E_i \rangle = \frac{1}{2} (E_{i+1} - E_{i-1}) \quad (22)$$

Figure 3 shows a plot of $g(E)$ as a continuous curve and $S(E)$ as a series of points.

Qualitatively the points (quantal results) follow the shape of the curve (Hénon and Heiles classical trajectory results). The two sets of results cannot hope to agree quantitatively since the sum $S(E)$ corresponds to volumes of phase space while the integral is for areas. However the energy at which the eigenvalues first become sensitive to the changing perturbation ($\approx 0.74D$) agrees well with the critical energy of Hénon and Heiles ($\approx 0.68D$).

Figure 3



The integral curve $J(E) = \int_0^E a_I(E) dE$ as a function of the energy E . The points correspond to the sum $S(E) = \frac{1}{D} \sum_i^E n_I(E_i) \langle \Delta E_i \rangle$.

Section 3 : Conclusions .

Eigenvalues of the Hénon and Héiles non-separable Hamiltonian with energy less than a critical energy $E^c \approx 0.74D$ were found to be insensitive to a slight change in the perturbation. These eigenvalues belong to a regular spectrum. Above the critical energy which is known to within a narrow band of energy, eigenvalues are found which are sensitive to a small change in the perturbation. These eigenvalues belong to an irregular spectrum.

Polyatomic molecules are examples of non-separable Hamiltonian systems. The results presented in this chapter support the prediction of Percival that the vibrational energy spectrum of polyatomic molecules will show a regular progression which will terminate abruptly at a maximum energy below the dissociation limit.

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CHAPTER 5Section 1 : Introduction.

The remainder of this thesis describes how semiclassical methods based on EBKM quantization and a classical variational principle can be used to determine bound states of model potentials of one and two degrees of freedom. These methods promise to be effective for the determination from potential surfaces of large numbers of vibrational energy levels of suitable polyatomic molecules at energies intermediate between equilibrium and dissociation.

The spectra of some diatomic molecules have already been observed for energy levels from the ground level to dissociation and semiclassical methods based on the well-known RKR (Rydberg-Klein-Rees) method have been used very effectively in relating the observations to potential energy curves through the Sommerfeld-Wilson rule

$$I = \frac{1}{2\pi} \oint p dq = (v + \frac{1}{2}) \hbar \quad (1)$$

The bound states of polyatomic systems can be investigated using related methods.

Section 2 : Methods for multidimensional spectra.

First successful attempts to obtain the energy spectra of multidimensional non-separable systems using semiclassical methods were made by Eastes and Marcus [1] and by Noid and Marcus [2]. They obtain toroids for quantization by explicit numerical integration of

trajectories. Level curves on Poincaré surfaces-of-section are constructed from numerical integration of Hamilton's equations of motion for given initial conditions. Particular surfaces-of-section can be chosen such that the level curves are topologically equivalent to independent closed curves on a toroid. Integration along the level curves yields the action integrals for the toroid

$$I_k = \frac{1}{2\pi} \oint \sum_{r=1}^N p_r dq_r \quad . \quad (2)$$

Only for certain energies (eigenvalues) will the I_k have the required form for quantization;

$$I_k = (v_k + \frac{1}{2}) \hbar \quad (v_k = 0, 1, 2, \dots) \quad . \quad (3)$$

An interpolation procedure is then used on a grid of values $I_k(E)$ to obtain energy levels $E_k(I_k = (v_k + \frac{1}{2})\hbar)$.

The accuracy of calculated energy levels depends on how much effort is put into the integration and interpolation procedures. If the number of degrees of freedom, N , is greater than two, then the above method for obtaining accurate energy levels can be time consuming.

Chapman, Garret and Miller [3] have recently developed a method for solving the classical Hamilton-Jacobi equation for multi-dimensional non-separable systems in terms of action-angle variables. Their approach is essentially that of Born's classical perturbation theory [4].

The total Hamiltonian is written as

$$H = H^0 + b_1 V \quad (4)$$

where the action-angle variables $(\underline{I}^0, \underline{\theta}^0)$ of the unperturbed H^0 are known. New variables $(\underline{I}, \underline{\theta})$ are sought such that the energy function for the full Hamiltonian depends only on the new action variables \underline{I} . Quantization of the action variables through equation (3) immediately gives the energy levels. The generator $S(\underline{I}, \underline{\theta}^0)$ of the transformation to the new set of variables is found by an iterative solution of the Hamilton-Jacobi equation using a Fourier representation in the space of the unperturbed angle variables $\underline{\theta}^0$.

Section 3 : Assumptions of the Semiclassical method.

A different method for obtaining toroids for quantization is preferred in this thesis. A stationary principle is used once to obtain iteration equations for toroids, and once for the energy levels derived from the toroids [5]. Accurate energy levels can therefore be obtained from less accurate toroids. A representation in the space of the perturbed angle variables is used, in marked contrast to Miller et al.. This should make the stationary method to be described shortly more general than Miller's method.

The following simplifying assumptions are made about a polyatomic molecule:

(SA1) There are no significant deviations from the Born-Oppenheimer approximation.

(SA2) There is a single potential energy surface V belonging to a single non-degenerate electronic state.

(SA3) V has only one minimum and no other stationary points.

(SA4) All effects of rotation can be neglected: The angular momentum is zero.

None of these assumptions is absolutely necessary for the application of semiclassical methods but they avoid complications which divert attention from the central features of the semiclassical method. The assumptions can be removed later.

One assumption that is necessary for the application of the methods to be described is

(SA5) The spectrum is regular.

This has been described in Chapter 3.

With the above assumptions the problem is reduced to the study of the quantization of non-separable systems with N degrees of freedom and a smooth potential function which has a minimum and no other stationary points in the region of interest.

Some of the properties of the classical motion for such a system have already been discussed. It will be convenient to present an alternative discussion of these properties with special emphasis on the invariant toroids which play an essential role in the quantization.

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CHAPTER 6Section 1: Classical vibrations of a diatomic molecule.

Consider the classical vibration of a diatomic molecule with the assumptions SA1 - SA4 given in Chapter 5. For coordinate q of relative motion of the nuclei and conjugate momentum p the Hamiltonian is $H(p, q)$. For a given energy between the equilibrium and dissociation energies the equation

$$H(p, q) = E \quad (1)$$

defines p as a two valued function of q which may be represented as a graph in the two-dimensional phase space of points $\underline{x} = (p, q)$ as illustrated in figure 1. This graph is the phase space trajectory and occupies the entire one-dimensional energy shell of points in phase space which satisfy equation (1).

Section 2: Classical vibrations of a polyatomic molecule.

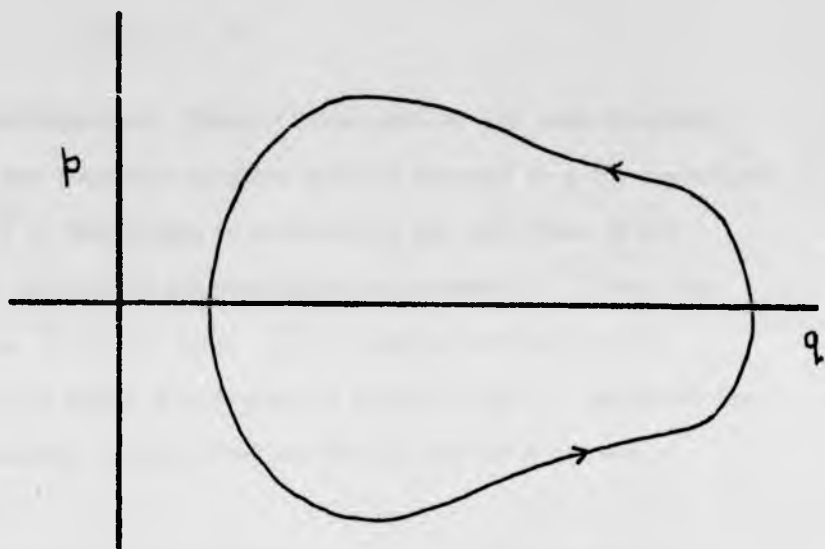
For a polyatomic molecule of N degrees of freedom the classical motion near equilibrium is close to that of N independent harmonic oscillators in normal coordinates of q_k with conjugate momenta p_k and characteristic angular frequencies

$$\omega_k = 2\pi / T_k \quad (2)$$

where T_k is a characteristic period.

Temporarily neglect all anharmonic coupling and consider only two degrees of freedom, such as the stretch modes q_1, q_2 of a

Figure 1



Phase space trajectory for vibration of diatomic molecule.

linear triatomic molecule. The phase space of points

$$\underline{X} = (\underline{p}, \underline{q}) = (p_1, p_2, q_1, q_2) \quad (3)$$

is four-dimensional. For energy E the energy shell defined by the equation

$$H(\underline{p}, \underline{q}) = E \quad (4)$$

is three-dimensional. Energy is conserved in each mode separately, so that the trajectory in phase space is confined to a two-dimensional region Σ . This region is invariant in the sense that if the molecule starts with its coordinates and momenta in Σ then they remain in Σ for all time. Σ is named an invariant toroid whatever the number N of degrees of freedom. Table 1 summarizes the dimensionality of various regions for two and for N degrees of freedom.

The semiclassical quantization of systems of N degrees of freedom requires the theory of action-angle variables.

For the vibrations of a diatomic molecule, for each value of the action variable I , the dependence of the point $\underline{X} = (p, q)$ in phase space on the angle variable θ ,

$$\underline{X}_{\Sigma}(\theta) = [p_2(\theta), q_2(\theta)] \quad (5)$$

provides a parametric definition of the trajectory or energy shell, and each in this case is equivalent to the invariant toroid Σ in one dimension.

TABLE 1

Region	Dimension for two degrees of freedom	Dimension for N degrees of freedom
Phase space	4	$2N$
Energy shell	3	$2N - 1$
Invariant toroid	2	N
Trajectory	1	1

Dimensions for two and for N degrees of freedom.

In N dimensions a toroid Σ is defined parametrically by the functional dependence of a point $\underline{X} = (\underline{p}, \underline{q})$ in phase space on the vector angle variable $\underline{\theta} = (\theta_1, \theta_2, \dots, \theta_N)$, that is

$$\begin{aligned} \underline{X}_{\Sigma}(\underline{\theta}) &= [p_{1\Sigma}(\underline{\theta}), q_{1\Sigma}(\underline{\theta})] \\ &= [p_{1\Sigma}(\theta_1, \theta_2, \dots, \theta_N), p_{2\Sigma}(\theta_1, \theta_2, \dots, \theta_N), \dots, p_{N\Sigma}(\theta_1, \theta_2, \dots, \theta_N), \\ &\quad q_{1\Sigma}(\theta_1, \theta_2, \dots, \theta_N), q_{2\Sigma}(\theta_1, \theta_2, \dots, \theta_N), \dots, q_{N\Sigma}(\theta_1, \theta_2, \dots, \theta_N)] \quad (6) \end{aligned}$$

It is not essential to consider the time explicitly, but it helps to make the connection with the more familiar theory of Hamilton's equations by using the linear relations

$$\theta_k = \omega_k t + \delta_k \quad (7)$$

between the time t on a given classical trajectory which lies on the toroid and the angle variable θ_k . In this equation δ_k is a phase that determines the location of a particular trajectory on the toroid. It follows from equation (7) that the total time derivative along a trajectory is given by

$$\frac{d}{dt} = \sum_{k=1}^N \omega_k \frac{\partial}{\partial \theta_k} \quad (8)$$

and this is used in the next chapter to obtain Hamilton's equations.

Returning to the linear triatomic molecule, suppose now that the amplitude of stretching is so large that there is significant anharmonic

coupling between the stretch modes. The total energy E is still conserved but the energy in each vibrational mode is not. In the terminology of classical dynamics the system is "non-integrable".

Kolmogorov, Arnol'd and Moser (KAM, [1]) proved that there are regions of phase space named the regular regions for which the trajectories are confined to invariant toroids, and numerical experiment [2] on model potentials that crudely resemble those of triatomic molecules indicate that the regular regions occupy a significant fraction of the phase space below a typical threshold energy. The remaining irregular regions and the properties of the corresponding energy levels have been discussed in Chapter 2. The remainder of this thesis is concerned with the regular regions only.

The properties of the invariant toroids for non-integrable or non-separable systems are similar to those of separable systems, and they can still be defined parametrically by equation (6). But the definition of the values of the action variables I_k must be based on Einstein's invariant definition [3].

$$I_k = \frac{1}{2\pi} \oint_{\gamma_k} \sum_{r=1}^N p_r dq_r \quad (9)$$

which has already been explained in Chapter 1 of this thesis. With this definition each toroid is labelled by N action variables (I_1, I_2, \dots, I_N) and by conservation of energy every point on the toroid has the same value E for the Hamiltonian function $H(\underline{p}, \underline{q})$. Within the regular region the toroids therefore define a function

$$E(I_1, I_2, \dots, I_N) = E(\underline{I}) \quad (10)$$

which will be used later for the determination of the regular semiclassical energy spectrum.

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CHAPTER 7Section 1: Variational Principles of Trkal and Van Vleck.

In quantum mechanics the variational principle for the energy can be used to derive perturbation expansions for the bound state wave functions and to obtain expressions for energy levels having errors which are of higher order than the errors in the wave functions.

An invariant toroid is the classical analogue of a bound state wave function and can be used to approximate both wave functions and energy levels. The variational principle for the energy of an invariant toroid is analogous to the variational principle for the energy of a wave function; this and further analogies are presented in Table 1.

Trkal [1] proposed a variational principle for action integrals without apparently realising that the variations need not be constrained to solutions of Hamilton's equations. Trkal showed that the total (classical) energy of a conservative dynamical system of N degrees of freedom which is separable in the coordinates and whose motion is multiply periodic can be expressed as

$$E = \sum_{k=1}^N \omega_k I_k - \bar{L} \quad (1)$$

I_k denotes the phase integral

$$I_k = \frac{1}{2\pi} \oint p_k dq_k \quad (2)$$

TABLE I

Quantal	Classical
1. Bound state wave function $\psi(\underline{q})$	Invariant toroid $\underline{X}(\underline{\theta}) = [q_{tor}(\underline{\theta}), p_{tor}(\underline{\theta})]$
2. Variational principle for mean energy of ψ	Variational principle for mean energy on $\underline{X}(\underline{\theta})$.
3. $\langle \psi H \psi \rangle$	$\oint' d\tau_0 H(q(\underline{\theta}), p(\underline{\theta})) = \langle H \rangle$
4. Fixed normalization integral $\mathcal{N} = \langle \psi \psi \rangle$	Fixed action integrals $I_k = \oint' d\tau_0 p(\underline{\theta}) \cdot \delta q(\underline{\theta}) / \delta \theta_k,$ $k = 1, 2, \dots, N$
5. Energy $E = \langle \psi H \psi \rangle / \langle \psi \psi \rangle$	Angular frequencies $\omega_k = \delta \langle H \rangle / \delta I_k, k = 1, 2, \dots, N$
6. Dynamical operator A	Function of coordinates and momenta $A(q, p)$ (sometimes called a 'phase function')
7. Schrödinger equation for bound states $(E - H)\psi = 0$	Angle form of Hamilton's equations $\sum_k \omega_k \frac{\partial}{\partial \theta_k} q(\underline{\theta}) = \frac{\partial H(q(\underline{\theta}), p(\underline{\theta}))}{\partial p}$ $\sum_k \omega_k \frac{\partial}{\partial \theta_k} p(\underline{\theta}) = -\frac{\partial H(q(\underline{\theta}), p(\underline{\theta}))}{\partial q}$
8. Quantal perturbation theory for hamiltonian operator $H = H^0 + b_1 V$	Classical perturbation theory for hamiltonian function $H(q, p) = H^0(q, p) + b_1 V(q, p)$ (normally V is a function of \underline{q} alone)
9. Unperturbed wave function ψ^0	Unperturbed toroid $\underline{X}^0(\underline{\theta})$
10. Unperturbed energy E^0	Unperturbed frequency vector $\underline{\omega}^0$
11. No degeneracy	No non-trivial small integers τ_k such that $\sum_k \tau_k \omega_k = 0.$

Analogies between quantal and classical mechanics of systems with N degrees of freedom.

\bar{L} denotes the mean of the Lagrangian function

$$L = T - V \quad (3)$$

where T and V are the kinetic and potential energies respectively. Trkal further showed that quantization of the energy (1) results from the following variational principle

$$\delta \Psi = 0 \quad \left(\begin{array}{l} \text{variations constrained} \\ \text{to solutions of} \\ \text{Hamilton's equations} \end{array} \right) \quad (4)$$

where

$$\Psi = \sum_{k=1}^N (v_k + \frac{1}{2}) \hbar \omega_k - \bar{L} \quad (5)$$

Van Vleck [2] realised that the variations need not be constrained to solutions of Hamilton's equations. He considered a dynamical system specified by N generalised coordinates q_k ($k = 1, 2, \dots, N$), each of which can be expanded as a multiple Fourier series for all values of the time:

$$q_k(t) = \sum_{\tau_1, \tau_2, \dots, \tau_N}^{\infty} B_{\tau_1, \tau_2, \dots, \tau_N}^{(k)} \exp\{i2\pi(\tau_1\omega_1 + \tau_2\omega_2 + \dots + \tau_N\omega_N)t\} \quad (6)$$

With functional Ψ defined by Trkal and given by equation (5), Van Vleck found that Hamilton's equations of classical mechanics are satisfied if

$$\delta \Psi = 0 \quad \left(\begin{array}{l} \text{amplitudes } B \text{ varied,} \\ \text{frequencies } \omega \text{ held} \\ \text{fast} \end{array} \right) \quad (7)$$

Furthermore the Sommerfeld-Wilson quantum conditions are equivalent to the restriction

$$\delta \Psi = 0 \quad \left(\begin{array}{l} \text{amplitudes } B \text{ held fast,} \\ \text{frequencies } \omega \text{ varied} \end{array} \right) \quad (8)$$

Hence Van Vleck was able to deduce that $\delta \Psi = 0$ for any variations of the coordinates which can be produced by altering either the amplitudes or the frequencies in the multiple Fourier expansion of these coordinates. Van Vleck writes ".....

$$\delta \Psi = 0 \quad \left(\begin{array}{l} \text{amplitudes and \\ \text{frequencies varied \\ \text{arbitrarily, without} \\ \text{regard to dynamics} \end{array} \right) \quad (9)$$

embodies all the demands of the classical dynamics and the quantum conditions and is therefore the quantum theory version of Hamilton's principle for a (multiply) periodic system".

Van Vleck's variational principle is an improvement on Trkal's, but it is still incomplete: In many dimensions time was used instead of the angle variables θ_k and the variations were implicitly restricted by an inadequate definition of action integral which is ambiguous for approximate toroids. Percival [3] proposed a variational principle for invariant toroids which is free from these restrictions.

Section 2 : Percival's Variational Principle

To formulate the variational principle, an integral of a function $f(\underline{\theta})$ over the entire space of the angle variables is defined by

$$\oint d\tau_{\theta} f(\underline{\theta}) = \int_{-\pi}^{\pi} d\theta_1 \int_{-\pi}^{\pi} d\theta_2 \cdots \int_{-\pi}^{\pi} d\theta_N f(\theta_1, \theta_2, \dots, \theta_N) \quad (10)$$

and a normalized integral by

$$\oint' d\tau_{\theta} f(\underline{\theta}) = (2\pi)^{-N} \oint d\tau_{\theta} f(\underline{\theta}) \quad (11)$$

When a toroid Σ (which need not be invariant) is defined parametrically by a phase space function

$$\chi_{\Sigma}(\underline{\theta}) = [q_{\Sigma}(\underline{\theta}), p_{\Sigma}(\underline{\theta})] \quad (12)$$

the mean value of the energy on the toroid is

$$\langle E \rangle_{\Sigma} = \oint' d\tau_{\theta} H(q_{\Sigma}(\underline{\theta}), p_{\Sigma}(\underline{\theta})) \quad (13)$$

and the mean value of the k^{th} action integral, defined for an arbitrary toroid is

$$I_k(\Sigma) = \oint' d\tau_{\theta} p_{\Sigma}(\underline{\theta}) \cdot \frac{\partial}{\partial \theta_k} q_{\Sigma}(\underline{\theta}) \quad (14)$$

This last definition is required because Einstein's definition in

terms of $\oint_{\theta_k} p \cdot dq$ along curves around the toroid is no longer valid

for arbitrary toroids; it depends on the curve.

For simplicity we now drop the arguments Σ . By analogy with the stationary principle for bound state solutions of the Schrödinger wave equation, Percival requires that the mean energy (13) should be stationary with respect to small smooth periodic variations in $\underline{q}(\underline{\theta})$, $\underline{p}(\underline{\theta})$ subject to the action integrals (14) remaining fixed; that is

$$\delta \bar{\Phi} = \mathcal{O}(\delta x)^2 \quad (15)$$

where

$$\bar{\Phi} = \oint d\tau_{\theta} \left(H(\underline{q}(\underline{\theta}), \underline{p}(\underline{\theta})) - \sum_{k=1}^N \omega_k \underline{p} \cdot \frac{\partial}{\partial \theta_k} \underline{q}(\underline{\theta}) \right) \quad (16)$$

for arbitrary variations

$$\delta \underline{\chi}(\underline{\theta}) = [\delta \underline{q}(\underline{\theta}), \delta \underline{p}(\underline{\theta})] \quad (17)$$

The ω_k are here just Lagrange multipliers. Equations (15), (16) and (17) express Percival's variational principle in Hamiltonian form. The analogy with the variational principle of Van Vleck which was written in Lagrangian form and expressed in equations (1), (5) and (9) is clear.

By the usual variational methods, equating coefficients of $\underline{q}(\underline{\theta})$ and $\underline{p}(\underline{\theta})$ to zero and ignoring terms of second order in the variations, the stationarity of the functional $\bar{\Phi}$ yields the

equations

$$\sum_{k=1}^N \omega_k \frac{\partial}{\partial \theta_k} \underline{q} = \frac{\partial}{\partial \underline{p}} H \quad (18)$$

$$\sum_{k=1}^N \omega_k \frac{\partial}{\partial \theta_k} \underline{p} = - \frac{\partial}{\partial \underline{q}} H \quad (19)$$

where

$$\frac{\partial}{\partial \underline{q}} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial q_N} \right); \quad \frac{\partial}{\partial \underline{p}} = \left(\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \dots, \frac{\partial}{\partial p_N} \right) \quad (20)$$

These equations are partial differential equations for a toroid. Percival names them the angle Hamilton's equations. If the Lagrange multipliers ω_k are identified with angular frequencies and the relation (8) of Chapter 6 for $\frac{d}{dt}$ is used, then the equations reduce to the more usual Hamilton's equations for a system on a trajectory which remains on the toroid. Thus the trajectory of any system with Hamiltonian function $H(\underline{q}, \underline{p})$ which starts at a point $(\underline{q}, \underline{p})$ on the toroid remains on the toroid for all time. It is in this sense that the toroid is invariant.

When the Hamiltonian function has the form

$$H = \frac{1}{2} \sum_k p_k^2 + V(\underline{q}) \quad (21)$$

the action integrals (14) can be written as

$$I_k = \sum_r G_{kr} \omega_r \quad (22)$$

where G_{kr} is an element of a generalised moment of inertia tensor,
given by

$$G_{kr} = \oint d\tau_{\theta} \frac{\partial q}{\partial \theta_k} \cdot \frac{\partial q}{\partial \theta_r} \quad (23)$$

Equations (22) and (23) will be used in Chapter 8 as part of an
iteration scheme for toroids.

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CHAPTER 8

Section 1: Quantization.

The EBKM theory of quantization applied to the main regular region for the vibration of polyatomic molecules gives the quantization rule

$$I_k = \left(\nu_k + \frac{1}{2} \right) \hbar \quad \begin{array}{l} (k = 1, 2, \dots, N) \\ (\nu_k = 0, 1, 2, \dots) \end{array} \quad (1)$$

where I_k is the invariant action integral as defined by Einstein and as it appears in the variational principle for invariant toroids (Chapter 7, equation (14)), and N is the number of degrees of freedom. The regular energy levels are found by substituting equation (1) into the energy function $E(I_1, I_2, \dots, I_N)$:

$$E_{\nu_1, \nu_2, \dots, \nu_N} = E \left(\left(\nu_1 + \frac{1}{2} \right) \hbar, \left(\nu_2 + \frac{1}{2} \right) \hbar, \dots, \left(\nu_N + \frac{1}{2} \right) \hbar \right) \quad (2)$$

$(\nu_k = 0, 1, 2, \dots)$

Thus the semiclassical energy levels can be obtained directly from the energy function of the action variables.

The variational principle for invariant toroids can be used to derive a number of different methods of quantization based on the equation (2). The principle will be used in two distinct ways:

- (1) To obtain equations for approximate toroids
- (2) To derive relatively accurate energy functions from approximate toroids.

Section 2 : Derivation of non-linear iteration equations.

An approximation to an invariant toroid is obtained by restricting it to a specific functional form and then applying a variational principle which preserves that form. The finite Fourier sum is an example of such a functional form.

Consider for simplicity two stretch modes of a linear triatomic molecule, with canonical coordinates and momenta $(\underline{r}, \underline{p}) = (x, y, p_x, p_y)$ and units chosen such that the Hamiltonian has the form

$$\begin{aligned} H(\underline{r}, \underline{p}) &= \frac{1}{2}(p_x^2 + p_y^2) + V(x, y) \\ &= \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 V^{\text{anh}}(x, y) \end{aligned} \quad (3)$$

The coordinates and momenta can be expanded in Fourier series which may be truncated for an approximation.

$$\underline{r}(\theta_1, \theta_2) = \sum_{\tau_1, \tau_2} \underline{r}_{\tau_1, \tau_2} \exp\{i(\tau_1 \theta_1 + \tau_2 \theta_2)\} \quad (4)$$

$$\underline{p}(\theta_1, \theta_2) = \sum_{\tau_1, \tau_2} i(\tau_1 \omega_1 + \tau_2 \omega_2) \underline{r}_{\tau_1, \tau_2} \exp\{i(\tau_1 \theta_1 + \tau_2 \theta_2)\} \quad (5)$$

The classical functional Φ defined in equation (16) of Chapter 7 becomes

$$\begin{aligned} \Phi &= \frac{1}{2} \sum_{\tau_1, \tau_2} (\tau_1 \omega_1 + \tau_2 \omega_2)^2 (x_{\tau_1, \tau_2} x_{-\tau_1, -\tau_2} + y_{\tau_1, \tau_2} y_{-\tau_1, -\tau_2}) \\ &\quad + \int d\tau_\theta V \left(\sum_{\tau_1, \tau_2} \underline{r}_{\tau_1, \tau_2} \exp\{i(\tau_1 \theta_1 + \tau_2 \theta_2)\} \right) \\ &\quad - \omega_1 I_1 - \omega_2 I_2 \end{aligned} \quad (6)$$

In this equation the action integrals I_1, I_2 are given by the matrix equation

$$\underline{I} = \underline{G} \underline{\omega} \quad (7)$$

with

$$G_{11} = \sum_{\tau_1, \tau_2} \tau_1^2 |\underline{r}_{\tau_1, \tau_2}|^2, \quad G_{22} = \sum_{\tau_1, \tau_2} \tau_2^2 |\underline{r}_{\tau_1, \tau_2}|^2$$

and

$$G_{12} = G_{21} = \sum_{\tau_1, \tau_2} \tau_1 \tau_2 |\underline{r}_{\tau_1, \tau_2}|^2. \quad (8)$$

Coefficients of the derivatives of the functional with respect to $x_{-\tau_1, \tau_2}$ and $y_{-\tau_1, \tau_2}$ are all zero, so that

$$(\tau_1 \omega_1 + \tau_2 \omega_2)^2 \underline{r}_{\tau_1, \tau_2} = -\underline{F}_{\tau_1, \tau_2} \quad (9)$$

where $\underline{F}_{\tau_1, \tau_2}$ are the Fourier components of the force:

$$\underline{F}(\underline{r}) = -\underline{\nabla} V(\underline{r}) \quad (10)$$

$$\underline{F}_{\tau_1, \tau_2} = \oint' d\tau_\theta \left[\exp\{-i(\tau_1 \theta_1 + \tau_2 \theta_2)\} \right] \underline{F}(x(\theta), y(\theta)). \quad (11)$$

The non-linear equations (9) may be written as

$$[\lambda - (\tau_1 \omega_1 + \tau_2 \omega_2)^2] x_{\tau_1, \tau_2} = \underline{F}_{x_{\tau_1, \tau_2}}^{\text{anh}}$$

$$[\mu - (\tau_1 \omega_1 + \tau_2 \omega_2)^2] y_{\tau_1, \tau_2} = \underline{F}_{y_{\tau_1, \tau_2}}^{\text{anh}}. \quad (12)$$

Here $\tilde{F}_{\tau_1, \tau_2}^{anh}(\underline{r})$ are the Fourier components of the anharmonic force

$$\tilde{F}_{\underline{r}}^{anh} = -b_i \nabla V^{anh}(\underline{r}) \quad (13)$$

Equations (12) can be used as a basis for a numerical iteration scheme which provides toroids without the necessity of determining action integrals. The action integrals appear as input parameters to the iteration scheme and remain fixed throughout the iteration.

Section 3 : A numerical iteration scheme .

Start with a solution of the harmonic problem without \tilde{F}^{anh} and assume the solution is real:

$$\begin{aligned} x_{1,0} &= x_{-1,0} = A_x \\ y_{0,1} &= y_{0,-1} = A_y \end{aligned} \quad (14)$$

with

$$A_x = \sqrt{\frac{I_1}{2\lambda^{1/2}}} \quad \text{and} \quad A_y = \sqrt{\frac{I_2}{2\mu^{1/2}}}$$

for chosen I_1, I_2 .

Use equations (12) for these components to obtain corrected frequencies at each step of the iteration as follows:

$$\begin{aligned} \omega_1^2 &= \lambda - \tilde{F}_{x_{1,0}}^{anh} / A_x \\ \omega_2^2 &= \mu - \tilde{F}_{y_{0,1}}^{anh} / A_y \end{aligned} \quad (15)$$

At each step use the remaining equations to obtain the Fourier

components of position from those of the anharmonic force:

$$x_{\tau_1, \tau_2} = F_{x_{\tau_1, \tau_2}}^{anh} / [\lambda - (\tau_1 \omega_1 + \tau_2 \omega_2)^2] \quad (\tau_1, \tau_2) \neq (\pm 1, 0)$$

$$y_{\tau_1, \tau_2} = F_{y_{\tau_1, \tau_2}}^{anh} / [\mu - (\tau_1 \omega_1 + \tau_2 \omega_2)^2] \quad (\tau_1, \tau_2) \neq (0, \pm 1) \quad (16)$$

Obtain the force components F_{τ_1, τ_2}^{anh} at each step from the position components r_{τ_1, τ_2} of the previous step through the sequence

$$r_{\tau_1, \tau_2} \rightarrow r(\theta_1, \theta_2) \rightarrow F_{\tau_1, \tau_2}^{anh}(\theta_1, \theta_2) \rightarrow F_{\tau_1, \tau_2}^{anh} \quad (17)$$

To determine the corrected fundamental Fourier components of the position, $x_{\pm 1, 0}$ and $y_{0, \pm 1}$, equations (7) and (8) are rearranged so as to separate out the contribution to the action integrals from the fundamental components of position. That is,

$$I \approx G_{11}^C \omega_1 + G_{22}^R \omega_2 \quad (18)$$

where $G_{11}^C = \sum_{\substack{\tau_1, \tau_2 \\ \neq (\pm 1, 0)}} \tau_1^2 |r_{\tau_1, \tau_2}|^2$, $G_{22}^C = \sum_{\substack{\tau_1, \tau_2 \\ \neq (0, \pm 1)}} \tau_2^2 |r_{\tau_1, \tau_2}|^2$

$$G_{11}^R = 2|r_{\pm 1, 0}|^2, \quad G_{22}^R = 2|r_{0, \pm 1}|^2$$

and

$$G_{12}^C = G_{21}^C = \sum_{\tau_1, \tau_2} \tau_1 \tau_2 |r_{\tau_1, \tau_2}|^2 \quad (19)$$

$$G_{12}^R = G_{21}^R = 0$$

The corrected fundamental components of position are given by

$$x_{\pm 1, 0} = \sqrt{(I_1 - \sum_{j=1}^2 G_{1j}^C \omega_j) / 2\omega_1 - y_{\pm 1, 0}^2}$$

$$y_{0, \pm 1} = \sqrt{(I_2 - \sum_{j=1}^2 G_{2j}^C \omega_j) / 2\omega_2 - x_{0, \pm 1}^2} \quad (20)$$

The mean energy on an approximate toroid specified by the action integrals I_1, I_2 is given by

$$\begin{aligned} \langle E \rangle &= \oint' d\tau_\theta H(x(\underline{\theta}), y(\underline{\theta}), p_x(\underline{\theta}), p_y(\underline{\theta})) \\ &= \oint' d\tau_\theta \left[\frac{1}{2}(p_x^2(\underline{\theta}) + p_y^2(\underline{\theta})) + \frac{1}{2}(\lambda x^2(\underline{\theta}) + \mu y^2(\underline{\theta})) \right. \\ &\quad \left. + b_1 V^{\text{anh}}(x(\underline{\theta}), y(\underline{\theta})) \right] \quad (21) \end{aligned}$$

where $x(\underline{\theta}), y(\underline{\theta})$ are obtained at some stage of the iteration cycle defined above. The mean energy on a converged toroid, calculated from equation (21) is an energy level of the Hamiltonian H if the chosen action integrals I_1, I_2 are such that

$$I_k = (v_k + \frac{1}{2})\hbar \quad (k=1,2) \quad (22)$$

Section 4 : An iteration scheme for energy functions.

To calculate energy functions for toroids an iteration scheme similar to the one above can be described. It is used in the next chapter to obtain expressions for energy levels for some model one- and two-dimensional systems. Within the new scheme it is necessary to calculate the action integrals I_1, I_2 at each stage of the iteration.

Start with the harmonic solution

$$\begin{aligned} x_{\pm 1,0} &= A_x \\ y_{0,\pm 1} &= A_y \end{aligned} \quad (23)$$

At each step of the iteration equations (15), (16) and (20) are used to obtain Fourier components of position x_{τ_1, τ_2} , y_{τ_1, τ_2} . Substitution of these components into equation (21) then yields an expression for the mean energy of an approximate toroid as a function of A_x, A_y . The same Fourier components when substituted into the equations

$$I_k = \oint d\tau_\theta \left(p_x(\theta) \frac{\partial x(\theta)}{\partial \theta_k} + p_y(\theta) \frac{\partial y(\theta)}{\partial \theta_k} \right) \quad (k=1,2) \quad (24)$$

give action integrals which are also functions of A_x, A_y . Using the method of "reversion of series", [1], it is possible to find expressions for A_x, A_y as functions of I_1, I_2 and substitution of these expressions into the mean energy finally yields an energy function $E(I_1, I_2)$.

It should be noticed that in obtaining the energy function $E(I_1, I_2)$ the variational principle is used twice, once for obtaining the equations (15), (16) and (20) to iterate, and once during the iteration to evaluate the mean energy (21). Accurate energy functions can therefore be quickly derived from less accurate toroids.

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CHAPTER 9

Section 1: Analytic Perturbation-Variation Methods.

This section describes how the iteration schemes devised in the previous chapter were used to obtain expressions for the energy levels of simple one- and two-dimensional model potentials.

In the equations of the iteration scheme described in section 4 of the previous chapter the anharmonic term was treated as a perturbation with parameter b_1 . For the potentials

$$V_1 = \frac{1}{2} \lambda x^2 + b_1 x^4 \quad (1)$$

$$V_2 = \frac{1}{2} (\lambda x^2 + \mu y^2) + b_1 xy \quad (2)$$

$$V_3 = \frac{1}{2} (\lambda x^2 + \mu y^2) + b_1 x^2 y^2 \quad (3)$$

a perturbation series for the coordinates was obtained to second order in b_1 for the one-dimensional potential V_1 , and to first order in b_1 for the two-dimensional potentials V_2 and V_3 . By using the stationary property of the functional $\bar{\Phi}$ the resulting energy functions $E(I)$ were obtained to fifth order in b_1 for V_1 and to third order in b_1 for V_2 and V_3 . A skeleton calculation of the energy function for V_1 is shown in appendix 2.

For potential V_1 with $\lambda = 1$,

$$\begin{aligned} x(\theta) = & A_x \left(1 - 3b_1 A_x^2 + \frac{303}{8} b_1^2 A_x^4 \right) \exp \{ i\theta \} \\ & + \frac{1}{2} b_1 A_x^3 \left(1 - \frac{39}{2} b_1 A_x^2 \right) \exp \{ i3\theta \} + \frac{1}{4} b_1^2 A_x^5 \exp \{ i5\theta \} \\ & + \text{complex conjugate (c.c.)} \end{aligned} \quad (4)$$

and

$$E(I) = I + \frac{3}{2} b_1 I^2 - \frac{17}{4} b_1^2 I^3 + \frac{375}{16} b_1^3 I^4 - \frac{10689}{64} b_1^4 I^5 + \frac{184125}{128} b_1^5 I^6 \quad (5)$$

An approximate expression for the energy levels E_v supported by the potential V_1 is given by

$$E_v = E\left(\left(\nu + \frac{1}{2}\right)\hbar\right) \quad (\nu = 0, 1, 2, \dots) \quad (6)$$

The result (5) can be compared with the energy function obtained by applying quantal perturbation theory (QPT) to the potential V_1 . To third order in b_1 ,

$$E^{\text{QPT}}(I) = I + \frac{3}{2} b_1 \left(I^2 + \frac{1}{4}\right) - \frac{17}{4} b_1^2 \left(I^3 + \frac{134}{17} I\right) + \frac{375}{16} b_1^3 \left(I^4 + \frac{569}{250} I^2 + \frac{513}{2000}\right) \quad (7)$$

where for purposes of comparison units have been chosen such that

$\hbar = 1$ and

$$I = \left(\nu + \frac{1}{2}\right) \quad (8)$$

Similarly, for the two-dimensional separable potential V_2 the coordinates $x(\underline{\theta})$, $y(\underline{\theta})$ to first order in b_1 are

$$x(\theta_1, \theta_2) = A_x \exp\{i\theta_1\} + \frac{b_1}{(\mu-1)} A_y \exp\{i\theta_2\} + \text{c.c.} \quad (9)$$

$$y(\theta_1, \theta_2) = -\frac{b_1}{(\mu-1)} A_x \exp\{i\theta_1\} + A_y \exp\{i\theta_2\} + \text{c.c.} \quad (10)$$

and the energy function $E(I)$ to third order in b_1 is

$$E(I_1, I_2) = I_1 + I_2 \mu^{k_2} - \frac{b_1^2}{2(\mu-1)} \left(I_1 - \frac{I_2}{\mu^{k_2}} \right) \quad (11)$$

Approximate energy levels E_{v_1, v_2} are obtained from equation (11) by using the relation

$$E_{v_1, v_2} = E\left(\left(v_1 + \frac{1}{2}\right)k_1, \left(v_2 + \frac{1}{2}\right)k_2\right) \quad (v_1, v_2 = 0, 1, 2, \dots) \quad (12)$$

Once again the result (11) can be compared with the energy function obtained by quantal perturbation theory. To third order in b_1 ,

$$E^{\text{QPT}}(I_1, I_2) = I_1 + I_2 \mu^{k_2} - \frac{b_1^2}{2(\mu-1)} \left(I_1 - \frac{I_2}{\mu^{k_2}} \right) \quad (13)$$

where

$$I_k = \left(v_k + \frac{1}{2}\right)k \quad (k=1, 2); \quad (v_k = 0, 1, 2, \dots) \quad (14)$$

Finally, for the two-dimensional non-separable potential V_3

$$\begin{aligned} x(\theta_1, \theta_2) = & A_x (1 - b_1 A_y^2) \exp\{i\theta_1\} + \frac{b_1}{2\mu^{k_2}(\mu^{k_2+1})} A_x A_y^2 \exp\{i(\theta_1 + 2\theta_2)\} \\ & + \frac{b_1}{2\mu^{k_2}(\mu^{k_2-1})} A_x A_y^2 \exp\{i(\theta_1 - 2\theta_2)\} + \text{c.c.} \end{aligned} \quad (15)$$

$$\begin{aligned} y(\theta_1, \theta_2) = & A_y \left(1 - \frac{b_1}{\mu} A_x^2\right) \exp\{i\theta_2\} + \frac{b_1}{2(\mu^{k_2+1})} A_x^2 A_y \exp\{i(2\theta_1 + \theta_2)\} \\ & - \frac{b_1}{2(\mu^{k_2-1})} A_x^2 A_y \exp\{i(2\theta_1 - \theta_2)\} + \text{c.c.} \end{aligned} \quad (16)$$

The energy function $E(I)$ to third order in b_1 is

$$E(I_1, I_2) = I_1 + I_2 \mu^{1/2} + \frac{b_1}{\mu^{1/2}} I_1 I_2 - b_1^2 \left(\frac{(3\mu-2)}{4\mu^{3/2}(\mu-1)} I_1^2 I_2 + \frac{(2\mu-3)}{4\mu(\mu-1)} I_1 I_2^2 \right) \\ + b_1^3 \left(\frac{(5\mu^2-5\mu+2)}{4\mu^{5/2}(\mu-1)^2} I_1^3 I_2 + \frac{3(\mu^2-3\mu+1)}{2\mu^2(\mu-1)^2} I_1^2 I_2^2 + \frac{(5-5\mu+2\mu^2)}{4\mu^{3/2}(\mu-1)^2} I_1 I_2^3 \right) \quad (17)$$

Quantal perturbation theory to second order in b_1 gives

$$E^{\text{QPT}}(I_1, I_2) = I_1 + I_2 \mu^{1/2} + \frac{b_1}{\mu^{1/2}} I_1 I_2 \\ - b_1^2 \left(\frac{(3\mu-2)}{4\mu^{3/2}(\mu-1)} I_1^2 I_2 + \frac{(2\mu-3)}{4\mu(\mu-1)} I_1 I_2^2 - \frac{3I_1}{16\mu(\mu-1)} + \frac{3I_2}{16\mu^{1/2}(\mu-1)} \right) \quad (18)$$

The above analysis shows that for the potentials V_1 , V_2 and V_3 defined in equations (1), (2) and (3) respectively, the perturbation-variation iteration scheme of the previous chapter provides energy functions as power series in the expansion parameter b_1 . For potentials V_1 and V_3 each term of the semiclassical series is exactly given by the dominant contribution to the corresponding term of the quantal series: Each term in the quantal series has a further expansion in powers of \hbar which is not recovered by the iteration schemes set out in this thesis. For the quadratic separable potential V_2 , the semiclassical and quantal perturbation series were found to be identical as expected.

Section 2 : Numerical Perturbation-Variation methods.

"Exact" semiclassical energy levels for potentials V_1 and V_3 were calculated using the numerical iteration scheme of chapter 8, section 3. For the one-dimensional potential V_1 the parameter b_1 was chosen so that the number of bound states was approximately the number of vibrational energy levels of iodine. Similarly for V_3 , μ and b_1 were chosen so that the number of bound states was typical of the stretch modes of a linear triatomic molecule, chosen to be carbon dioxide.

Fourier analysis of the periodic functions employed NAG library subroutine CO6ABF as basis. For one degree of freedom each singly periodic function $f_1(\theta)$ of the angle variables was approximated by a finite Fourier sum of M terms. The functions f_1 were tabulated at M equally spaced points in $-\pi < \theta \leq \pi$. For two degrees of freedom each doubly periodic function $f_2(\theta_1, \theta_2)$ was approximated by a finite double Fourier sum of M^2 terms and the functions f_2 were tabulated on an $M \times M$ mesh spanning the space of the angle variables $-\pi < \theta_1 \leq \pi, -\pi < \theta_2 \leq \pi$.

The iterations were considered to be successfully completed when the difference between successive values of the mean energy was less than some tolerable error TOL.

Section 3 : Numerical Quantal methods.

Exact quantal energy levels for V_1 and V_3 were also calculated so that a comparison with the corresponding semiclassical energy levels could be made. The exact quantal levels were found by diagonalizing the relevant Hamiltonian matrices. For this purpose

matrix elements of the Hamiltonians with potentials V_1 and V_3 were calculated using harmonic oscillator (Hermite polynomial) wave functions as bases. Non zero matrix elements of V_1 and V_3 are

$$(x^4)_{\nu, \nu} = \frac{3}{2} \left[\left(\nu + \frac{1}{2}\right)^2 + \frac{1}{4} \right] \quad (19)$$

$$(x^4)_{\nu, \nu \pm 2} = \left(\nu + \frac{1}{2} \pm 1\right) \left[\left(\nu + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu + \frac{1}{2} \pm \frac{3}{2}\right) \right]^{\frac{1}{2}}$$

$$(x^4)_{\nu, \nu \pm 4} = \frac{1}{4} \left[\left(\nu + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu + \frac{1}{2} \pm \frac{3}{2}\right) \left(\nu + \frac{1}{2} \pm \frac{5}{2}\right) \left(\nu + \frac{1}{2} \pm \frac{7}{2}\right) \right]^{\frac{1}{2}}$$

$$(x^2 y^2)_{\nu_1, \nu_2; \nu_1, \nu_2} = \frac{1}{2\mu^{\frac{1}{2}}} (\nu_1 + \frac{1}{2}) (\nu_2 + \frac{1}{2})$$

$$(x^2 y^2)_{\nu_1, \nu_2; \nu_1, \nu_2 \pm 2} = \frac{1}{2\mu^{\frac{1}{2}}} (\nu_1 + \frac{1}{2}) \left[\left(\nu_2 + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu_2 + \frac{1}{2} \pm \frac{3}{2}\right) \right]^{\frac{1}{2}} \quad (20)$$

$$(x^2 y^2)_{\nu_1, \nu_2; \nu_1 \pm 2, \nu_2} = \frac{1}{2\mu^{\frac{1}{2}}} (\nu_2 + \frac{1}{2}) \left[\left(\nu_1 + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu_1 + \frac{1}{2} \pm \frac{3}{2}\right) \right]^{\frac{1}{2}}$$

$$(x^2 y^2)_{\nu_1, \nu_2; \nu_1 \pm 2, \nu_2 \pm 2} = \frac{1}{4\mu^{\frac{1}{2}}} \left[\left(\nu_1 + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu_1 + \frac{1}{2} \pm \frac{3}{2}\right) \left(\nu_2 + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu_2 + \frac{1}{2} \pm \frac{3}{2}\right) \right]^{\frac{1}{2}}$$

$$(x^2 y^2)_{\nu_1, \nu_2; \nu_1 \pm 2, \nu_2 \mp 2} = \frac{1}{4\mu^{\frac{1}{2}}} \left[\left(\nu_1 + \frac{1}{2} \pm \frac{1}{2}\right) \left(\nu_1 + \frac{1}{2} \pm \frac{3}{2}\right) \left(\nu_2 + \frac{1}{2} \mp \frac{1}{2}\right) \left(\nu_2 + \frac{1}{2} \mp \frac{3}{2}\right) \right]^{\frac{1}{2}}$$

For each diagonalization a sufficient number of basis functions (order of matrix) was chosen to ensure convergence of any tabulated energy level to 0.01 cm for the worst case.

Section 4 : Results.

Table 1 compares the lowest 18 exact quantal energy levels supported by V_1 with the corresponding exact semiclassical energy levels, and also with the approximate semiclassical energy levels obtained from equations (5) and (7) with $\frac{t}{h} = 1$. A similar comparison is shown in table 2 for the lowest 45 energy levels of V_3 .

For the two-dimensional system the agreement between exact quantal and exact semiclassical seems to be better than for the one-dimensional system. It is possible to understand why this is so by comparing the quantal energy function (18) with the semiclassical expression (17): For V_3 the quantal and semiclassical perturbation series are identical through first order in the expansion parameter b_1 whereas for V_1 there is a difference $\frac{3}{8}b_1$ between the quantal and semiclassical first order energies. If the quantity $\frac{3}{8}b_1$ is regarded as a first order quantal correction to the semiclassical energy levels of V_1 and is added to equation (5) then the results are much improved. (Table 1)

While the results of the above numerical experiments show excellent agreement between the semiclassical and quantal energy levels, it is certainly a valid criticism that even for the highest energy levels tabulated, the displacements of the eigenvalues from their unperturbed harmonic values are quite small. A more severe test of the semiclassical method is needed.

Further numerical experiments were performed on the Hamiltonian

$$H = \frac{1}{2} (p_x^2 + p_y^2) + \frac{1}{2} (\lambda x^2 + \mu y^2) + b_1 x (y^2 + b_2 x^2) \quad (21)$$

Table 1

Semiclassical and Quantal energy levels of the one-dimensional Hamiltonian

$$H = \frac{1}{2} (p_x^2) + \frac{1}{2} \lambda x^2 + b_1 x^4 ; \quad \lambda = 1, \quad b_1 = -0.0015$$

Dissociation energy = 12102.5 cm⁻¹

Uncoupled ($b_1 = 0$) cm ⁻¹	Quantum N ⁰ (v)	Semiclassical			Quantal
		Approx. Analytic cm ⁻¹	Exact [†] cm ⁻¹	Exact + $\frac{3b_1}{8a}$ cm ⁻¹	Exact cm ⁻¹
145.22	0	145.06	145.06	144.89	144.89
435.66	1	434.18	434.18	434.02	434.01
726.10	2	721.97	721.97	721.81	721.80
1016.54	3	1008.41	1008.41	1008.25	1008.24
1306.98	4	1293.48	1293.48	1293.32	1293.31
1597.42	5	1577.17	1577.17	1577.00	1576.99
1887.86	6	1859.44	1859.44	1859.28	1859.26
2178.30	7	2140.29	2140.29	2140.13	2140.10
2468.74	8	2419.69	2419.69	2419.52	2419.50
2759.18	9	2697.61	2697.61	2697.45	2697.42
3049.62	10	2974.04	2974.04	2973.88	2973.84
3340.06	11	3248.95	3248.95	3248.79	3248.75
3630.50	12	3522.32	3522.32	3522.15	3522.11
3920.94	13	3794.11	3794.11	3793.95	3793.90
4211.38	14	4064.31	4064.31	4064.15	4064.09
4501.82	15	4332.89	4332.88	4332.71	4332.65
4792.26	16	4599.80	4599.79	4599.62	4599.56
5082.70	17	4865.03	4865.01	4864.84	4864.78

Table 2

Semiclassical and Quantal energy levels of the two-dimensional non-separable Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x^2 y^2$$

$$\lambda = 1, \mu = 0.5, b_1 = -0.003$$

$$\text{Dissociation Energy} = 58817.9 \text{ cm}^{-1}$$

Uncoupled ($b_1 = 0$) cm^{-1}	Quantum N^{OS} (ν_1, ν_2)	Semiclassical		Quantal
		Approx. Analytic cm^{-1}	Exact cm^{-1}	Exact cm^{-1}
1204.79	0,0	1203.29	1203.29	1203.29
2202.87	0,1	2198.35	2198.35	2198.35
2516.29	1,0	2611.78	2611.78	2611.77
3200.96	0,2	3193.38	3193.38	3193.39
3614.37	1,1	3600.78	3600.78	3600.78
4027.79	2,0	4020.26	4020.26	4020.23
4199.03	0,3	4188.38	4188.39	4188.40
4612.46	1,2	4589.70	4589.70	4589.70
5025.87	2,1	5003.18	5003.19	5003.16
5197.07	0,4	5183.36	5183.35	5183.39
5439.29	3,0	5428.73	5428.73	5428.70
5610.53	1,3	5578.54	5578.54	5578.54
6023.96	2,2	5935.98	5985.97	5985.96
6195.20	0,5	6178.31	6178.30	6178.35
6437.37	3,1	6405.56	6405.56	6405.53
6608.61	1,4	6567.29	6567.29	6567.30
6850.79	4,0	6837.19	6837.19	6837.15
7022.06	2,3	6968.63	6968.63	6968.63

Table 2 (Cont'd.)

Uncoupled ($b_1 = 0$) cm ⁻¹	Quantum N ^{OS} . (ν_1, ν_2)	Semiclassical		Quantal
		Approx. Analytic cm ⁻¹	Exact cm ⁻¹	Exact cm ⁻¹
7193.27	0,6	7173.22	7173.21	7173.27
7435.46	3,2	7382.20	7382.20	7382.19
7606.70	1,5	7555.96	7555.96	7556.01
7848.87	4,1	7807.90	7807.90	7807.87
8020.11	2,4	7951.15	7951.15	7951.15
8191.36	0,7	8168.10	8168.10	8168.15
8262.29	5,0	8245.64	8245.64	8245.59
8433.53	3,3	8358.66	8358.66	8358.65
8604.77	1,6	8544.53	8544.53	8544.56
8846.96	4,2	8778.38	8778.39	8778.52
9018.20	2,5	8933.52	8933.51	8933.52
9189.44	0,8	9162.96	9162.94	9163.02
9260.37	5,1	9210.21	9210.21	9210.16
9431.61	3,4	9334.92	9334.93	9334.91
9602.86	1,7	9533.01	9532.99	9533.03
9673.79	6,0	9654.08	9654.08	9654.02
9845.03	4,3	9748.62	9748.62	9748.58
10016.27	2,6	9915.74	9915.73	9915.74
10187.52	0,9	10157.78	10157.75	10157.83
10258.46	5,2	10174.51	10174.50	10174.46
10429.70	3,5	10310.98	10310.98	10310.96
10600.94	1,8	10521.40	10521.36	10521.42

Table 2 (Cont'd.)

<u>Uncoupled ($b_1 = 0$)</u> cm ⁻¹	<u>Quantum N^{OS}.</u> <u>(v_1, v_2)</u>	<u>Semiclassical</u>		<u>Quantal</u>
		<u>Approx. Analytic</u> cm ⁻¹	<u>Exact</u> cm ⁻¹	<u>Exact</u> cm ⁻¹
10671.87	6,1	10612.49	10612.49	10612.43
10843.11	4,4	10718.61	10718.61	10718.58
11014.36	2,7	10897.80	10897.78	10897.80
11085.29	7,0	11062.50	11062.50	11062.43
11256.53	5,3	11138.51	11138.50	11138.46

Eastes and Marcus [1] and also Noid and Marcus [2] were the first workers to successfully apply a semiclassical technique to the problem of determining the energy levels of multidimensional non-separable systems, and they concentrated their efforts on hamiltonian (21). Chapman Garrett and Miller [3] have also been able to determine semiclassical energy levels of (21) using a method which is due to Born [4] .

Tables 3 and 4 present the results of applying the numerical iteration procedure described in chapter 8 to the cubic hamiltonian (21). A test of the semiclassical method is therefore made under conditions of strong as well as weak perturbations.

For the worst case, $M = 16$ was sufficient to yield energy levels which had converged to within $TOL = 0.0001$ in four iterations. The semiclassical energy levels are identical with those obtained by Miller et al.. Any discrepancy in table 3 with the results of Marcus et al is almost certainly due to a lack of sufficient computation in the calculations of the group.

Section 5: Conclusions

The semiclassical iteration procedures of this thesis have been shown to be effective for the determination of the energy levels of a range of one and two dimensional hamiltonian functions. Corresponding quantal methods become impractical when applied to molecules with more than two atoms especially if many energy levels are desired. It is expected that semiclassical techniques will have to be used in such cases and it remains to be shown whether the methods of this thesis will be effective when applied to molecules.

Table 3

Semiclassical eigenvalues of the non-separable Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x(y^2 + b_2 x^2) \quad k = 1.$$

λ, μ b_1, b_2	Escape Energy D	Quantum N ^{OS} . (ν_1, ν_2)	Semiclassical eigenvalues				Quantal
			Ref. 2	Ref. 3	Ref. 4	Present	
0.29375, 2.12581 -0.1116, 0.08414	5.2106	0,0	0.9920	0.9922	0.9920	0.9920	0.9916
		1,1	1.5164	1.5164	1.5164	1.5164	1.5159
		2,0	2.0313	2.0313	2.0313	2.0313	2.0308
		0,1	2.4196	2.4198	2.4194	2.4194	2.4188
0.49, 1.69 -0.1, 0.1	11.4601	0,0	0.9955	0.9954	0.9955	0.9955	0.9955
		1,0	1.6870	1.6870	1.6870	1.6870	1.6870
		0,1	2.2780	2.2785	2.2782	2.2782	2.2781
		2,0	2.3750	2.3751	2.3750	2.3750	2.3750
		1,1	2.9584	2.9588	2.9584	2.9584	2.9583
			-	3.5480	3.5480	3.5480	3.5479

TOL = 0.0001

M ≤ 16

Table 4

Semiclassical eigenvalues of the non-separable Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x(y^2 + b_2 x^2)$$

$$\lambda = 0.49, \quad \mu = 1.69, \quad b_2 = -b_1; \quad \hbar = 1$$

b_1	Escape Energy D	Semiclassical		Semiclassical		Semiclassical		Quantal
		Ref. 4	Present	Ref. 4	Present	Ref. 4	Present	
0	—	1.	1.	1.7	1.7	1.7	1.7	2.3
-.06	38.5375	.9987	.9987	1.6970	1.6970	1.6970	1.6970	2.2932
-.08	19.7919	.9975	.9975	1.6933	1.6933	1.6933	1.6933	2.2870
-.10	11.4601	.9955	.9955	1.6870	1.6870	1.6870	1.6870	2.2782
-.12	7.1204	.9927	.9927	1.6770	1.6770	1.6770	1.6769	2.2661
-.14	4.6157	.9889	.9889	1.6617	1.6617	1.6617	1.6612	2.2498

TOL = 0.0001

M ≤ 16

References

- [1] EASTES, W., and MARCUS, R. A., 1974, J. Chem. Phys., 61, 4301.
- [2] NOID, D. W., and MARCUS, R.A., 1975, J. Chem. Phys., 62, 2119.
- [3] CHAPMAN, S., GARRETT, B.C., and MILLER, W. H., 1976, J. Chem. Phys., 64,
502
- [4] BORN, M., 1960, "The Mechanics of the Atom" (Ungar).

APPENDIX 1Improved representation for the Hénon and Heiles energy surfaces

A representation is required for the energy surfaces of the Hénon and Heiles Hamiltonian

$$H = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} r^2 + \frac{b_1}{3} r^3 \sin 3\theta \quad (1)$$

It seems natural to consider the Hamiltonian

$$H^0 = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} r^2 \quad (2)$$

as forming a basis for the representation. This equation describes a two-dimensional harmonic oscillator with unit frequency. If an energy surface E of Hamiltonian (1) occupies a volume V of phase space then surfaces E^0 of (2) must be included in the basis so that the volume V is spanned. The fewer the number of surfaces E^0 required the better.

It is convenient to rewrite equation (1) as

$$H' \equiv H = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} \lambda r^2 + \frac{b_1}{3} r^3 \sin 3\theta + \frac{1}{2} (1-\lambda) r^2 \quad (3)$$

and to consider

$$H^{0'} = \frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) + \frac{1}{2} \lambda r^2 \quad (4)$$

as forming a new basis for the Hénon and Heiles Hamiltonian. Since equation (3) remains unaltered whatever is the value of λ , we can choose λ to be that value of the pulsance in equation (4) which minimizes the number of surfaces E^0 required to represent the energy surfaces of (3).

Figure 1 shows equipotential lines for H and for H^0 . On the equipotential E shown, the momentum is zero so we have

$$E = \frac{1}{2} r_{\max}^2 - \frac{b_1}{3} r_{\max}^3 \quad (5)$$

and

$$E = \frac{1}{2} r_{\min}^2 + \frac{b_1}{3} r_{\min}^3 \quad (6)$$

Otherwise, at a point r within the equipotential E ,

$$\frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right) = E - \frac{1}{2} r^2 - \frac{b_1}{3} r^3 \sin 3\theta \quad (7)$$

For fixed r , $\frac{1}{2} \left(p_r^2 + \frac{p_\theta^2}{r^2} \right)$ has extreme values when $\sin 3\theta = \pm 1$.

Case 1: $\sin 3\theta = -1$

$$E^{0'} = E - \frac{1}{2} (1-\lambda) r^2 + \frac{b_1}{3} r^3 \quad (8)$$

where

$$0 < r < r_{\max} \quad (9)$$

and r_{\max} is a solution of equation (5).

Case 2: $\sin 3\theta = +1$

$$E^{0'} = E - \frac{1}{2} (1-\lambda) r^2 - \frac{b_1}{3} r^3 \quad (10)$$

where

$$0 < r < r_{\min} \quad (11)$$

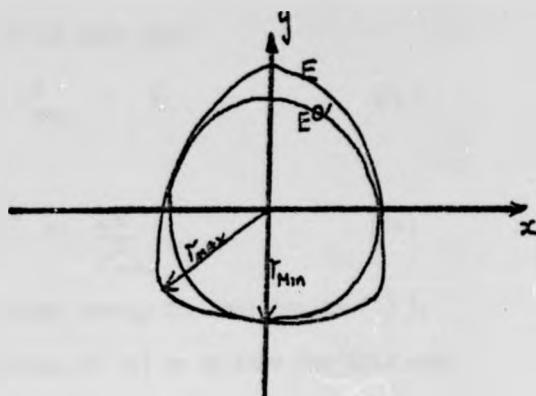
and r_{\min} is a solution of equation (6)

Figure 2 shows a schematic plot of equations (8) and (10).

The volume V^0 of phase space associated with the energy surface E^0 of equation (4) is well known to be

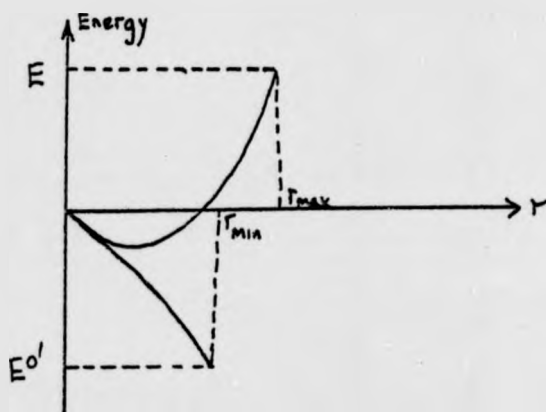
$$V^0 = \frac{\pi^2 E^{0'}{}^2}{4\lambda} \quad (12)$$

Figure 1



Equipotentials E and E' of hamiltonians H and H'

Figure 2



Schematic plot of equations (7) and (9).

Since we may never have $E^{0'} > E$ for fixed r , it follows from equation (8) that the optimum value of λ which minimizes the phase space volume (12) is such that

$$\frac{1}{2} \lambda r_{\max}^2 = E \quad (13)$$

i.e.

$$\lambda^{\text{opt}} = \frac{2E}{r_{\max}^2} \quad (14)$$

For $E = 1/6b_1^2$ (the escape energy for Hamiltonian (1)), $r_{\max} = 1/b_1$ is a solution of (5) so we have for this case

$$\lambda^{\text{opt}} = \frac{1}{3} .$$

APPENDIX 2

Skeleton calculation of energy function $E(I)$ for one-dimensional oscillator with quantic perturbation.

$$H = \frac{1}{2} (p_x^2 + \lambda x^2) + b_1 x^4 \quad ; \quad \lambda = 1, \quad \omega^{(0)} = \lambda^{\frac{1}{2}} = 1 \quad (1)$$

Start with zeroth order ($b_1=0$) solution

$$x^{(0)} = A_x \exp\{i\theta\} + \text{complex conjugate (c.c.)} \quad (2)$$

$$p_x^{(0)} = \omega^{(0)} \frac{dx^{(0)}}{d\theta} = i A_x \exp\{i\theta\} + \text{c.c.} \quad (3)$$

Action integral for zeroth order solution

$$I^{(0)} = \oint' d\tau_\theta p_x^{(0)} \frac{dx^{(0)}}{d\theta} = 2A_x^2 \quad (4)$$

Mean energy on first order toroid

$$\begin{aligned} \langle E \rangle &= \oint' d\tau_\theta H(x(\theta), p_x(\theta)) \\ &= 2A_x^2 + \frac{3}{2} b_1 (2A_x^2)^2 \end{aligned} \quad (5)$$

Energy function for first order toroid

$$E(I) = I + \frac{3}{2} b_1 I^2 \quad (6)$$

anharmonic Force

$$\begin{aligned} F^{\text{anh}}(x^{(0)}) &= -\frac{dV^{\text{anh}}}{dx} = -4b_1 x^{(0)3} \\ &= -4b_1 A_x^3 (3e^{i\theta} + e^{3i\theta}) + \text{c.c.} \end{aligned} \quad (7)$$

Frequency on first order toroid.

$$\omega^{(1)2} = \lambda - \frac{F_1^{\text{anh}}}{x_1^{(0)}} \quad (8)$$

$$= 1 + 6b_1 (2A_x^2)$$

$$\therefore \omega^{(1)} = 1 + 3b_1 (2A_x^2) \quad (9)$$

First order toroid

$$x_\tau^{(1)} = F^{\text{anh}} / [\lambda - \tau^2 \omega^{(1)2}] \quad (\tau \neq 1) \quad (10)$$

$$x_3^{(1)} = \frac{b_1 A_x}{4} (2A_x^2) \quad (11)$$

$$\text{Let } x_1^{(1)} = A_x (1 + \xi b_1 (2A_x^2)) \quad (12)$$

where ξ has to be determined from the constancy of the action integral I

With (11) and (12),

$$x^{(1)} = A_x (1 + \xi b_1 (2A_x^2)) \exp\{i\theta\} + \frac{b_1}{4} A_x (2A_x^2) \exp\{i3\theta\} + \text{cc.} \quad (13)$$

$$\therefore p_x^{(1)} = \omega^{(1)} \frac{dx^{(1)}}{d\theta}$$

$$= i A_x (1 + (3 + \xi) b_1 (2A_x^2)) \exp\{i\theta\}$$

$$+ i \frac{3b_1}{4} A_x (2A_x^2) \exp\{i3\theta\} + \text{cc.} \quad (14)$$

$$\therefore I^{(1)} = (2A_x^2) (1 + (3+2\xi) b_1 (2A_x^2)) \quad (15)$$

$$\therefore \text{Condition on } I^{(1)} \text{ gives } \xi = -\frac{3}{2}$$

We now have determined the first order toroid as

$$x^{(1)} = A_x \left(1 - \frac{3}{2} b_1 (2A_x^2) \right) \exp\{i\theta\} + \frac{b_1}{4} A_x (2A_x^2) \exp\{i3\theta\} + \text{c.c.}$$

$$p_x^{(1)} = i A_x \left(1 + \frac{3}{2} b_1 (2A_x^2) \right) \exp\{i\theta\} + i \frac{3b_1}{4} A_x (2A_x^2) \exp\{i3\theta\} + \text{c.c.} \quad (16)$$

Substitution of equations (16) into the equation for the mean energy

$$\langle E \rangle = \oint' d\tau_\theta H(x^{(1)}(\theta), p_x^{(1)}(\theta))$$

yields an energy function $E(I)$ correct to third order in b_1 . We can continue the above scheme until satisfied with the accuracy of the energy function.

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