

Vibrational quantization of polyatomic molecules

by I. C. PERCIVAL and N. POMPHREY

Department of Applied Mathematics, Queen Mary College,
Mile End Road, London E1 4NS

(Received 21 May 1975)

Semiclassical methods based on Einstein-Brillouin-Keller quantization and a classical variational principle are described. They are applied to model potentials of up to three 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.

1. INTRODUCTION

With present-day laser technology it has become practicable to investigate the higher vibrational levels of polyatomic molecules. There is no doubt that lasers will be used to extend observations to more transitions at higher precision and without the complications due to the rotational band structure [1]. It is possible that transitions involving a significant fraction of the vibrational levels of suitable triatomic molecules might be observed. For common triatomic molecules without H atoms there are usually thousands of vibrational levels for each electronic state.

For the low energy levels matrix methods and quantal perturbation theory have been effective in relating the levels obtained from observed spectra to trial potentials [2]. But both of these methods require a basis set of wave functions and for high vibrational levels all but a small proportion of this basis will be strongly coupled by anharmonic terms. The order of the matrices in the matrix method will be formidably high, as will be the order of perturbation in the perturbation method.

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 Rydberg-Klein-Rees method have been used very effectively in relating the observations to potential energy curves through the Bohr-Sommerfeld quantization rule

$$I = \frac{1}{2\pi} \oint p \, dq = (v + \frac{1}{2})h. \quad (1.1)$$

Semiclassical methods are particularly useful for the higher levels, where anharmonic terms are large.

Semiclassical methods have been used in the study of collisions between atoms and diatomic molecules [3] and look very promising. It is worth investigating the corresponding bound states of triatomic systems using related methods.

The application of the methods is not easy but model examples given here (§§ 5 and 6) suggest that they might be a useful complement to traditional methods.

We make the following simplifying assumptions :

- 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 semi-classical methods, but they avoid complications which divert attention from the central features of the method. The assumptions can be removed later.

One assumption which *is* necessary for the application of the methods we shall describe is

- SA5 The spectrum is regular.

This is described elsewhere [4, 11] and also in §§ 2 and 4.

With these assumptions the problem is reduced to the study of the quantization of 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.

The properties of the classical motion for such a system are described in § 2, where we introduce the ‘invariant toroids’. Section 3 contains a variational principle for invariant toroids which is analogous to the variational principle for the energy of bound quantal states [5].

In § 4 we describe the Einstein–Brillouin–Keller (E.B.K.) quantization rule and show how it is related to invariant toroids. Eastes and Marcus [6] have obtained toroids for quantization by explicit numerical integration of trajectories. This can be time-consuming and becomes very difficult when the number of degrees of freedom exceeds two.

A non-linear equation for the invariant toroids is obtained from the variational principle in § 4 and iteration schemes are described for the solution of this equation. The subsequent determination of energy levels is straightforward.

Section 5 contains numerical examples in which it is shown that the iteration schemes of § 4 can provide accurate toroids with comparatively little effort. Section 6 gives examples of the use of the methods of § 4 to obtain analytic expressions for the energy levels of a model one-dimensional and of a two-dimensional system. The results are compared, where possible, with quantal perturbation theory and matrix methods.

2. CLASSICAL MOTION

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

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

defines p as a two-valued function of q , which may be represented as a graph in the two-dimensional phase space of points $\mathbf{X} = (q, p)$ 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).

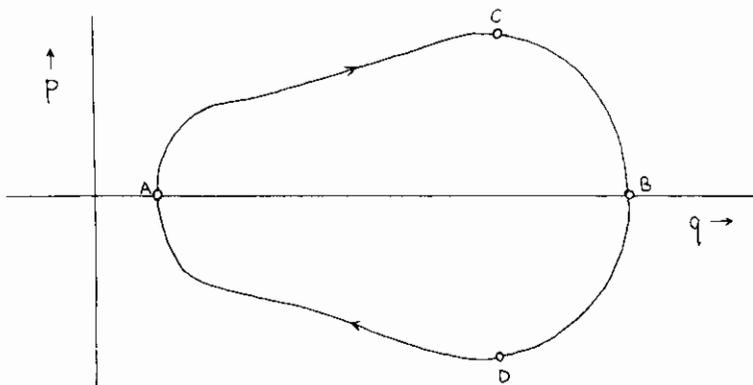


Figure 1. Phase-space trajectory for vibration of diatomic molecule.

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 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 linear triatomic molecule. The phase space of points

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

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

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

is three-dimensional. Energy is conserved for each mode separately, so 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 (\mathbf{q}, \mathbf{p}) in Σ , then they remain in Σ for all time. The shape of Σ resembles a doughnut or torus (figure 2) and it will be 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 [7] requires the theory of action-angle variables [8]. The classical action variable

$$I_k = \frac{1}{2\pi} \oint p_k dq_k \quad (5)$$

is conjugate to the angle variable θ_k which lies in the range

$$-\pi < \theta_k \leq \pi. \quad (6)$$

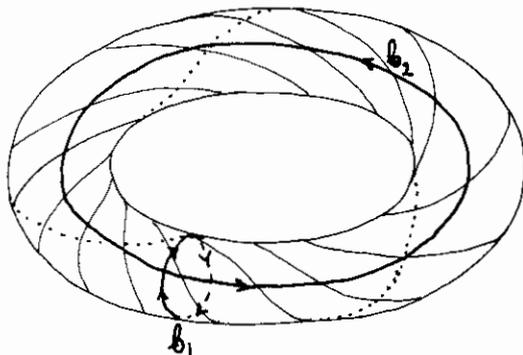


Figure 2. Phase space trajectory and invariant toroid for stretching of linear triatomic molecule. \mathcal{C}_1 and \mathcal{C}_2 are curves for the definition of action integrals I_1 and I_2 .

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

Table 1. Dimensions for two and for N degrees of freedom.

By definition *all* functions are periodic of period 2π in θ_k . Where notation of other authors differs from ours, the variables are related by the equations

$$J_k = 2\pi I_k, \quad w = \frac{\theta}{2\pi}. \quad (7)$$

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

$$\mathbf{X}_\Sigma(\theta) = [q_\Sigma(\theta), p_\Sigma(\theta)], \quad (8)$$

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.

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

$$\begin{aligned} \mathbf{X}_\Sigma(\boldsymbol{\theta}) &= [\mathbf{q}_\Sigma(\boldsymbol{\theta}), \mathbf{p}_\Sigma(\boldsymbol{\theta})] \\ &= [q_{1\Sigma}(\theta_1, \theta_2, \dots, \theta_N), q_{2\Sigma}(\theta_1, \theta_2, \dots, \theta_N), \dots, q_{N\Sigma}(\theta_1, \theta_2, \dots, \theta_N), \\ &\quad p_{1\Sigma}(\theta_1, \theta_2, \dots, \theta_N), p_{2\Sigma}(\theta_1, \theta_2, \dots, \theta_N), \dots, p_{N\Sigma}(\theta_1, \theta_2, \dots, \theta_N)] \quad (9) \end{aligned}$$

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

$$\theta_k = \omega_k t + \delta_k \quad (10)$$

between the time t on a given classical trajectory which lies in the toroid and the angle variable θ_k . In this equation ω_k is a characteristic angular frequency of the motion and δ_k is a phase shift that determines the location of a particular trajectory in the toroid. It follows from equation (10) that the total time derivative along a trajectory is given by

$$\frac{d}{dt} = \sum_{k=1}^N \omega_k \frac{\partial}{\partial \theta_k} \quad (11)$$

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

Returning to the linear triatomic molecule, suppose now that the amplitude of the 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'.

For the two degrees of freedom of the stretch modes it is not evident whether a given trajectory in phase space will still be confined to a two-dimensional toroid or whether it will wander throughout the three-dimensional energy shell.

It was proved by Kolmogorov, Arnol'd and Moser (K.A.M., [9]) that there are regions of phase space, named the *regular regions*, for which the trajectories are confined to invariant toroids, and it has been amply demonstrated by numerical experiment [10] on model potentials that crudely resemble those of triatomic molecules, 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 are discussed elsewhere [4, 11]; only the regular regions are considered here.

The properties of the invariant toroids for non-integrable systems are similar to those of separable systems, and they can still be defined parametrically by equation (9). But the definition of the values of the action variables I_k for an invariant toroid can no longer take the form of equation (5). This point is crucial to the problem of quantization. In their original form of the quantization rule, Sommerfeld and Wilson used equation (5) to define the action integrals. However, the definition depends on the choice of coordinates. Schwarzschild and Epstein [12] proposed a modification which was still not invariant under the canonical transformations of classical mechanics.

It was left to Einstein [13] to find a definition which does not require a particular choice of canonical coordinates. His definition is equivalent to

$$\begin{aligned} I_k &= \frac{1}{2\pi} \oint_{\mathcal{C}_k} \mathbf{p} \cdot d\mathbf{q} \\ &= \frac{1}{2\pi} \oint_{\mathcal{C}_k} \sum_{i=1}^N p_i dq_i \end{aligned} \quad (12)$$

and can be used for invariant toroids whether the hamiltonian is separable or not. The \mathcal{C}_k are independent curves on the toroid which cannot be deformed continuously into one another, as illustrated for two dimensions in figure 2. Einstein shows that the definition is independent of continuous transformations on the toroid, by analogy with the contours of complex integration theory.

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 $H(\mathbf{q}, \mathbf{p})$. Within the regular region the toroids therefore define a function

$$E(I_1, I_2, \dots, I_N) = E(\mathbf{I}). \quad (13)$$

This energy function is all that is needed to determine the regular semiclassical energy spectrum.

3. VARIATIONAL PRINCIPLE

Quantum mechanics is more familiar these days than is classical mechanics. It is well known that 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 2, which can be used as a guide to the classical theories.

Trkal [14] proposed a variational principle for action integrals without apparently realizing that the variations did not require to be constrained to solutions of Hamilton's equations. Van Vleck [15] realized that the variations need not be so constrained and proposed a variational principle which is the same as that presented here for one dimension. However, 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. His principle was, therefore, incomplete.

We use a variational principle for invariant toroids [5] which is free from these restrictions.

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

$$\oint d\tau_{\theta} f(\boldsymbol{\theta}) = \int_{-\pi}^{\pi} d\theta_1 \int_{-\pi}^{\pi} d\theta_2 \dots \int_{-\pi}^{\pi} d\theta_N f(\theta_1, \theta_2, \dots, \theta_N) \quad (14)$$

and a normalized integral by

$$\oint' d\tau_{\theta} f(\boldsymbol{\theta}) = (2\pi)^{-N} \oint d\tau_{\theta} f(\boldsymbol{\theta}). \quad (15)$$

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

$$\mathbf{X}_{\Sigma}(\boldsymbol{\theta}) = [\mathbf{q}_{\Sigma}(\boldsymbol{\theta}), \mathbf{p}_{\Sigma}(\boldsymbol{\theta})] \quad (16)$$

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

Table 2. Analogies between quantal and classical mechanics of systems with N degrees of freedom.

the mean value of the energy on the toroid is

$$\langle E \rangle_{\Sigma} = \oint' d\tau_{\theta} H(\mathbf{q}_{\Sigma}(\theta), \mathbf{p}_{\Sigma}(\theta)) \quad (17)$$

and the mean of the k th action integral, defined for an arbitrary toroid, is

$$I_k(\Sigma) = \oint' d\tau_{\theta} \mathbf{p}_{\Sigma}(\theta) \cdot \partial \mathbf{q}_{\Sigma}(\theta) / \partial \theta_k. \quad (18)$$

This last definition is required because Einstein's definition in terms of $\oint_{\mathcal{C}_k} \mathbf{p} \cdot d\mathbf{q}$ 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 and propose that the mean energy (17) should be stationary subject to the action integrals (18) remaining fixed; that is

$$\Delta\Phi = \mathcal{O}(\Delta x)^2, \quad (19)$$

where

$$\Phi = \oint' d\tau_\theta \left(H(\mathbf{q}(\theta), \mathbf{p}(\theta)) - \sum_{k=1}^N \omega_k \mathbf{p} \cdot \partial \mathbf{q} / \partial \theta_k \right) \quad (20)$$

for arbitrary variations

$$\Delta \mathbf{X}(\theta) = [\Delta \mathbf{q}(\theta), \Delta \mathbf{p}(\theta)]. \quad (21)$$

The ω_k are here just Lagrange multipliers.

By the usual variational methods, equating coefficients of $\Delta \mathbf{q}$, $\Delta \mathbf{p}$ to zero we obtain [5] the equations

$$\sum_k \omega_k \partial \mathbf{q} / \partial \theta_k = \partial H / \partial \mathbf{p}, \quad (22 a)$$

$$\sum_k \omega_k \partial \mathbf{p} / \partial \theta_k = -\partial H / \partial \mathbf{q}, \quad (22 b)$$

where

$$\frac{\partial}{\partial \mathbf{q}} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2}, \dots, \frac{\partial}{\partial q_N} \right); \quad \frac{\partial}{\partial \mathbf{p}} = \left(\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2}, \dots, \frac{\partial}{\partial p_N} \right). \quad (23)$$

These equations are partial differential equations for a toroid. They will be called the angle Hamilton's equations. If the Lagrange multipliers ω_k are identified with angular frequencies and the relation (11) for d/dt is used, then the equations reduce to the more usual Hamilton equations for a system on a trajectory which remains in the toroid. Thus the trajectory of any system with hamiltonian function $H(\mathbf{q}, \mathbf{p})$ which starts at a point (\mathbf{q}, \mathbf{p}) on the toroid remains on the toroid for all time. It is in this sense that the toroid is invariant.

In obtaining the variational principle, the corresponding quantal theory has been used as a guide, but there are some essential differences between the two theories. The classical theory is non-linear; this leads to difficulties when it comes to applying the theory. In particular, one is confronted with a problem which is known in celestial mechanics as the problem of small divisors and which is related to the problem of Fermi resonances in molecules. The non-linearity also leads to the irregular regions, where no toroids appear to exist, so that they cannot be found using a variational or any other method. It is unlikely that any semiclassical theory of the irregular spectrum exists except in a statistical sense, and we do not consider the irregular regions further.

4. QUANTIZATION AND METHODS

Einstein's 1917 paper [13], in which the invariant definition of I_k was introduced, treated the problem of quantization in the old quantum theory. The action integrals (12) were equated to integer multiples of \hbar .

Since 1925, molecular theory has been based on quantum mechanics, and the 'old' quantum theory reinterpreted as asymptotic quantum mechanics in the limit $\hbar \rightarrow 0$ and as a part of semiclassical mechanics. Brillouin [16] sketched

the semiclassical mechanics of systems with many degrees of freedom in 1926, and in 1958 Keller showed that corrections to the Einstein theory were required at caustics [17]. The whole Einstein-Brillouin-Keller (E.B.K.) theory of quantization was made rigorous and expressed in terms of phase space and invariant toroids by Maslov [18]. In the previous section we have used this phase-space picture consistently, even though the results were expressed by other authors in configuration space. The E.B.K. theory is valid only in the regular regions, though this has not always been stated.

The E.B.K. theory of quantization applied to the main regular region for the vibration of polyatomic molecules gives the quantization rule

$$I_k = (v_k + \frac{1}{2})\hbar \quad (k = 1, 2, \dots, N; v_k = 0, 1, 2, \dots), \quad (24)$$

where I_k is the invariant action integral as defined by Einstein and as it appears in the variational principle for invariant toroids, and N is the number of degrees of freedom.

The regular energy levels E_{v_1, v_2, \dots, v_N} are found by substituting equation (24) into the energy function (13)

$$E_{v_1, v_2, \dots, v_N} = E((v_1 + \frac{1}{2})\hbar, (v_2 + \frac{1}{2})\hbar, \dots, (v_N + \frac{1}{2})\hbar) \quad (v_k = 0, 1, 2, \dots). \quad (25)$$

It is assumed in this formula that the toroids of interest can be obtained by continuous deformation from those in the neighbourhood of equilibrium. This is normally true, and the exceptions would take us too far from our main theme. 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 equation (25). We use the principle in two distinct ways :

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

We consider two methods, both based on Fourier expansions of the coordinates and momenta which are truncated where necessary for an approximation. Consider for simplicity two stretch modes of a linear triatomic molecule, with canonical coordinates and momenta $(\mathbf{r}, \mathbf{p}) = (x, y, p_x, p_y)$ and units chosen such that the hamiltonian has the form

$$\begin{aligned} H(\mathbf{r}, \mathbf{p}) &= \frac{1}{2}(p_x^2 + p_y^2) + V(x, y) \\ &= \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda_x^2 + \mu_y^2) + b_1 V^{\text{anh}}(x, y). \end{aligned} \quad (26)$$

If the coordinates and momenta are expanded in Fourier series

$$\mathbf{r}(\theta_1, \theta_2) = \sum_{s_1, s_2} \mathbf{r}_{s_1, s_2} \exp i(s_1\theta_1 + s_2\theta_2), \quad (27 a)$$

$$\mathbf{p}(\theta_1, \theta_2) = \sum_{s_1, s_2} i(s_1\omega_1 + s_2\omega_2)\mathbf{r}_{s_1, s_2} \exp i(s_1\theta_1 + s_2\theta_2), \quad (27 b)$$

the classical functional Φ defined in equation (20) becomes

$$\begin{aligned} \Phi &= \frac{1}{2} \sum_{s_1, s_2} (s_1\omega_1 + s_2\omega_2)^2 (x_{s_1, s_2} x_{s_1, -s_2} + y_{s_1, s_2} y_{-s_1, -s_2}) \\ &\quad + \oint' d\tau_\theta V(\sum_{s_1, s_2} \mathbf{r}_{s_1, s_2} \exp i(s_1\theta_1 + s_2\theta_2)) - \omega_1 I_1 - \omega_2 I_2. \end{aligned} \quad (28)$$

The coefficients of the derivatives with respect to $x_{-s_1, -s_2}$ and $y_{-s_1, -s_2}$ are all zero, so that

$$(s_1\omega_1 + s_2\omega_2)^2 \mathbf{r}_{s_1, s_2} = -\mathbf{F}_{s_1, s_2}, \quad (29)$$

where \mathbf{F}_{s_1, s_2} are the Fourier components of the force

$$\mathbf{F}(\mathbf{r}) = -\nabla V(\mathbf{r}), \quad (30)$$

$$\mathbf{F}_{s_1, s_2} = \oint' d\tau_\theta [\exp -i(s_1\theta_1 + s_2\theta_2)] \mathbf{F}(x(\theta), y(\theta)). \quad (31)$$

The non-linear equations (29) may be written as

$$\left. \begin{aligned} [\lambda - (s_1\omega_1 + s_2\omega_2)^2] x_{s_1, s_2} &= F_{x_{s_1, s_2}}^{\text{anh}}, \\ [\mu - (s_1\omega_1 + s_2\omega_2)^2] y_{s_1, s_2} &= F_{y_{s_1, s_2}}^{\text{anh}}. \end{aligned} \right\} \quad (32)$$

Here $\mathbf{F}_{s_1, s_2}^{\text{anh}}$ are the Fourier components of the anharmonic force

$$\mathbf{F}^{\text{anh}}(\mathbf{r}) = -b_1 \nabla V^{\text{anh}}(\mathbf{r}). \quad (33)$$

Equation (32) can be used as a basis for an iteration scheme which provides toroids without the necessity of determining action integrals. Later, when we wish to obtain expressions for energy levels, the iteration scheme will be modified. We continue to work with two degrees of freedom but the method generalizes directly to three or more degrees of freedom.

Start with a solution of the harmonic problem without \mathbf{F}^{anh} . For the iteration assume that the fundamental components of x and y are fixed:

$$\left. \begin{aligned} x_{1, 0} = x_{-1, 0} &= A_x, \\ y_{0, 1} = y_{0, -1} &= A_y, \end{aligned} \right\} \quad (34)$$

and assume that the solution is real. Then use equations (32) for these components to obtain corrected frequencies at each step of the iteration as follows

$$\left. \begin{aligned} \omega_1^2 &= \lambda - \frac{F_{x_{1, 0}}^{\text{anh}}}{A_x}, \\ \omega_2^2 &= \mu - \frac{F_{y_{0, 1}}^{\text{anh}}}{A_y}. \end{aligned} \right\} \quad (35)$$

At each step use the remaining equations to obtain the Fourier components of position from those of the anharmonic force:

$$\left. \begin{aligned} x_{s_1, s_2} &= F_{x_{s_1, s_2}}^{\text{anh}} / [\lambda - (s_1\omega_1 + s_2\omega_2)^2] \quad (s_1, s_2) \neq (\pm 1, 0), \\ y_{s_1, s_2} &= F_{y_{s_1, s_2}}^{\text{anh}} / [\mu - (s_1\omega_1 + s_2\omega_2)^2] \quad (s_1, s_2) \neq (0, \pm 1). \end{aligned} \right\} \quad (36)$$

Obtain the force components $\mathbf{F}_{s_1, s_2}^{\text{anh}}$ at each step from the position components \mathbf{r}_{s_1, s_2} of the previous step through the sequence

$$\mathbf{r}_{s_1, s_2} \rightarrow \mathbf{r}(\theta_1, \theta_2) \rightarrow \mathbf{F}^{\text{anh}}(\theta_1, \theta_2) \rightarrow \mathbf{F}_{s_1, s_2}^{\text{anh}}.$$

Examples using this iteration scheme are given in § 5.

To calculate energy functions for toroids we describe an iteration scheme which is similar to the one above. It will be used in § 6 to obtain energy levels for some model systems. Within the new scheme it will be necessary to calculate the action integrals I_1, I_2 . Furthermore, these quantities are held fixed throughout the iteration whereas the fundamental components of x and y are not.

Start with the harmonic solution (34). At each step of the iteration use equations (35) and (36) to obtain Fourier components of position

$$x_{s_1, s_2}, (s_1, s_2) \neq (\pm 1, 0); \quad y_{s_1, s_2}, (s_1, s_2) \neq (0, \pm 1).$$

These Fourier components, together with the condition of holding the action integrals fixed, are sufficient to determine the corrected fundamental components of the position

$$x_{\pm 1, 0}, \quad y_{0, \pm 1}.$$

Use equation (17) to obtain a mean energy as a function of A_x, A_y :

$$\begin{aligned} \langle E \rangle &= \oint' d\tau_\theta H(x(\theta), y(\theta), p_x(\theta), p_y(\theta)) \\ &= \oint' d\tau_\theta \left(\frac{1}{2}(p_x^2(\theta) + p_y^2(\theta)) + \frac{1}{2}(\lambda x^2(\theta) + \mu y^2(\theta)) + b_1 V^{\text{anh}}(x(\theta), y(\theta)) \right), \end{aligned} \quad (37)$$

and equations (18) to obtain action integrals as functions of A_x, A_y :

$$I_k = \oint' d\tau_\theta \left(p_x(\theta) \frac{\partial x(\theta)}{\partial \theta_k} + p_y(\theta) \frac{\partial y(\theta)}{\partial \theta_k} \right) \quad (k = 1, 2). \quad (38)$$

Find A_x, A_y as functions of I_1, I_2 ('reversion of series') and on substituting into equation (37) for the mean energy, obtain an energy function $E(I_1, I_2)$.

It should be noticed that in obtaining the energy function $E(I_1, I_2)$ we use the variational principle *twice*, once for obtaining the equations (35), (36) to iterate, and once during the iteration to evaluate the mean energy (37).

5. NUMERICAL INTEGRATION AND TRAJECTORIES

In this method, which uses the first iteration scheme of § 4, the Fourier coefficients at each stage were obtained numerically. The iteration was considered to be successfully completed when the mean square differences of successive forces or positions was less than some tolerable error TOL. Trajectories $\mathbf{r}(\theta(t))$ obtained by the iteration procedure, known as the 'angle solution' were compared with step-by-step integration of Newton's equations of motion, the 'Newton solutions'.

For the angle solutions real Fourier analysis was used in practice. For two degrees of freedom each doubly periodic function $f(\theta_1, \theta_2)$ of the angle variables was approximated by a finite Fourier sum of $(2M+1)^2$ terms, M being the order of the highest component in each dimension. The functions f were tabulated where necessary on a $(2M+1) \times (2M+1)$ mesh.

The Newton solutions were obtained with a step size chosen to keep the magnitude of the error at each step well below a maximum of 10^{-8} .

For two and three degrees of freedom the potentials had the forms

$$V_2 = \frac{1}{2}(\lambda x^2 + \mu y^2 + b_1 x^2 y^2), \quad (39)$$

$$V_3 = \frac{1}{2}(\lambda x^2 + \mu y^2 + \nu z^2 + b_1 y^2 z^2 + b_2 z^2 x^2 + b_3 x^2 y^2). \quad (40)$$

The coefficients λ , μ , ν were chosen to be of order unity, ensuring that in the absence of the anharmonic terms the characteristic periods would be of order 2π . The sizes of the coupling coefficients were limited by the requirements of convergence, more severe for three than for two dimensions, and the ratios of $\lambda^{1/2}$, $\mu^{1/2}$ and $\nu^{1/2}$ were chosen as they were for the same reason. The phase shifts δ were chosen zero in every case, as a trivial change in the origin of time effectively covers a range of δ .

At a few instants in time, given in table 3 for different cases, the angle and Newton solutions were tabulated and compared. Results are presented in table 4 for two degrees of freedom and in table 5 for three degrees of freedom. The values of $\epsilon(100)$ and $\epsilon(1000)$ approximate the maximum of the magnitude of the difference between the tabulated angle and Newton solutions over about 100 and 1000 units of time respectively, that is about 14 or 140 characteristic periods of uncoupled motion.

Tabulation number	Times T of tabulation and of comparison
1	0(0.25)10(2.5)100
2	0(0.2)10(2.0)100(20)1000(0.2)1004
3	0(0.4)2; 10(0.4)12; 100(0.4)102; 1000(0.4)1003.2

Table 3. Tabulation times.

μ	b_1	A_x	A_y	$\log_{10}(\text{TOL})$	Required number of iterations	Tabulation number	$\log_{10}[\epsilon(100)]$	$\log_{10}[\epsilon(1000)]$
0.7071	0.2	1.0	0.5	-12	5	1	-6.5	
0.7071	0.5	1.0	0.5	-12	7	1	-6	
0.3331	0.5	1.0	0.5	-12	7	1	-6	
0.7071	0.5	1.0	0.5	-16	10	1	-7	
0.7071	0.5	1.0	0.5	-16	10	2	-7	-5.7
0.7071	0.5	1.0	0.5	-14	9	2	-7	-6
0.7071	0.5	0.9	0.5	-16	9	2	-7.5	-6.3
0.7071	0.5	0.8	0.5	-16	8	2	-7.7	-6.3
0.7071	0.5	0.1	0.05	-16	4	1	-9.5	

Table 4. Comparison of angle and Newton solutions for two degrees of freedom. $\lambda=1$ and M throughout.

In every case the angle and Newton solutions were in agreement to within 10^{-5} units of distance. This shows that even this crude numerical iteration procedure provides toroids which are excellent approximations to invariant toroids. In practice the time of computation for the iteration was less than that required for the numerical integration of the trajectories, so the method is very promising for the calculation of the energy function $E(\mathbf{I})$ and thus for semi-classical quantization.

ν	b_1	b_2	b_3	Highest component M	$\log_{10}(\text{TOL})$	Required number of iterations	Tabulation number	$\log_{10}[\epsilon(100)]$	$\log_{10}[\epsilon(10000)]$
0.5314	0.1	0.15	0.2	3	-12	7	2	-4	-3
0.5314	0.1	0.15	0.1	4	-12	6	3	-6	-4.7
0.5314	0.1	0.15	0.1	4	-14	8	3	-6	-5
1.9914	0.1	0.15	0.1	4	-14	6	3	-7	-6.3
1.9914	0.1	0.15	0.12	4	-14	5†	3	-6.7	
1.9914	0.1	0.15	0.08	4	-14	6	3	-6.7	-5.7
1.9914	0.119	0.178	0.095	4	-14	6	3	-6.7	
1.9914	0.15	0.2	0.115	4	-14	7	3	-6.5	-5.5
1.9914	0.178	0.238	0.137	4	-14	4†	3	-6.4	
1.9914	0.22	0.28	0.17	4	-14	7	3	-6.3	

† For this run modified Fourier coefficients of the previous run were used to start the iteration.

Table 5. Comparison of angle and Newton solutions for three degrees of freedom. For all runs $\lambda=1$, $\mu=2^{-1/2} \approx 0.7071$, $A_x=A_z=2$; $A_y=1$.

6. ANALYTIC PERTURBATION-VARIATION AND ENERGY LEVELS

In this section the feasibility of using the variational principle is approached from a different direction. In the iteration equations (35) to (38) the anharmonic term is treated as a perturbation with parameter b_1 , and for simple one-dimensional and two-dimensional potentials

$$V_1 = \frac{1}{2}\lambda x^2 + b_1 x^4, \quad (41)$$

$$V_2 = \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x^2 y^2, \quad (42)$$

a perturbation series for the coordinates is obtained to second order in b_1 for V_1 and to first order in b_1 for V_2 . By using the stationary property of the functional Φ the resulting energy functions $E(I)$ are obtained to fifth order in b_1 for V_1 and to third order in b_1 for V_2 .

For potential V_1 with $\lambda=1$ we find

$$x(\theta) = A_x(1 - 3b_1 A_x^2 + \frac{3}{8}b_1^2 A_x^4) \exp i\theta + \frac{1}{2}b_1 A_x^3(1 - \frac{3}{2}b_1 A_x^2) \exp 3i\theta \\ + \frac{1}{4}b_1^2 A_x^5 \exp 5i\theta + \text{complex conjugate (c.c.)} \quad (43)$$

and

$$E(I) = I + \frac{3}{2}b_1 I^2 - \frac{1}{4}b_1^2 I^3 + \frac{3}{16}b_1^3 I^4 - \frac{1}{64}b_1^4 I^5 + \frac{1}{128}b_1^5 I^6. \quad (44)$$

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

$$E_v = E((v + \frac{1}{2})\hbar) \quad (v=0, 1, 2, \dots). \quad (45)$$

We can compare the result (44) with the energy function obtained by applying quantal perturbation theory (Q.P.T.) to the potential V_1 . To third order in b_1 we find

$$E^{\text{Q.P.T.}}(I) = I + \frac{3}{2}b_1(I^2 + \frac{1}{4}) - \frac{1}{4}b_1^2(I^3 + \frac{1}{17}I) + \frac{3}{16}b_1^3(I^4 + \frac{5}{23}I^2 + \frac{5}{206}I), \quad (46)$$

where for purposes of comparison we have here put $\hbar=1$ and

$$I = (v + \frac{1}{2}). \quad (47)$$

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

$$x(\theta_1, \theta_2) = A_x(1 - b_1 A_y^2) \exp i\theta_1 + \frac{1}{2}b_1 \frac{A_x A_y^2}{\mu^{1/2}(\mu^{1/2} + 1)} \exp i(\theta_1 + 2\theta_2) \\ + \frac{1}{2}b_1 \frac{A_x A_y^2}{\mu^{1/2}(\mu^{1/2} - 1)} \exp i(\theta_1 - 2\theta_2) + \text{c.c.} \quad (48)$$

$$y(\theta_1, \theta_2) = A_y \left(1 - b_1 \frac{A_x^2}{\mu} \right) \exp i\theta_2 + \frac{1}{2}b_1 \frac{A_x^2 A_y}{(\mu^{1/2} + 1)} \exp i(2\theta_1 + \theta_2) \\ - \frac{1}{2}b_1 \frac{A_x^2 A_y}{(\mu^{1/2} - 1)} \exp i(2\theta_1 - \theta_2) + \text{c.c.} \quad (49)$$

and the energy function $E(\mathbf{I})$ to third order in b_1 is

$$E(I_1, I_2) = I_1 + I_2\mu^{1/2} + \frac{b_1 I_1 I_2}{\mu^{1/2}} - b_1^2 \left(I_1^2 I_2 \frac{(3\mu-2)}{4\mu^{3/2}(\mu-1)} + I_1 I_2^2 \frac{(2\mu-3)}{4\mu(\mu-1)} \right) \\ + b_1^3 \left(I_1^3 I_2 \frac{(5\mu^2-5\mu+2)}{4\mu^{5/2}(\mu-1)^2} + 3I_1^2 I_2^2 \frac{(\mu^2-3\mu+1)}{2\mu^2(\mu-1)^2} + I_1 I_2^3 \frac{(5-5\mu+2\mu^2)}{4\mu^{3/2}(\mu-1)^2} \right). \quad (50)$$

Approximate energy levels E_{r_1, r_2} are obtained from (50) by using the relation

$$E_{r_1, r_2} = E\left((v_1 + \frac{1}{2})\hbar, (v_2 + \frac{1}{2})\hbar\right) \quad (k=1, 2; v_k=0, 1, 2, \dots) \quad (51)$$

Once again we can compare the result (50) with the energy function obtained by quantal perturbation theory. To second order in b_1 we find

$$E^{Q.P.T.}(I_1, I_2) = I_1 + I_2\mu^{1/2} + \frac{b_1 I_1 I_2}{\mu^{1/2}} - b_1^2 \left(I_1^2 I_2 \frac{(3\mu-2)}{4\mu^{3/2}(\mu-1)} \right. \\ \left. + I_1 I_2^2 \frac{(2\mu-3)}{4\mu(\mu-1)} - \frac{3I_1}{16\mu(\mu-1)} + \frac{3I_2}{16\mu^{1/2}(\mu-1)} \right), \quad (52)$$

where

$$I_k = (v_k + \frac{1}{2}) \quad (k=1, 2; v_k=0, 1, 2, \dots). \quad (53)$$

The above analysis shows that for the potentials V_1, V_2 defined in equations (41), (42) respectively, the perturbation-variation iteration scheme of § 4 provides energy functions as power series in the expansion parameter b_1 . Each term of the series is given exactly by the dominant contribution to the corresponding term of the quantal perturbation series.

Exact energy levels	Semiclassical levels	Semiclassical + $\frac{3}{8}b_1$
144.89	145.06	144.90
434.01	434.18	434.02
721.80	721.97	721.81
1008.24	1008.41	1008.25
1293.31	1293.48	1293.32
1576.99	1577.17	1577.00
1859.26	1859.44	1859.28
2140.10	2140.29	2140.13
2419.50	2419.69	2419.52
2697.42	2697.61	2697.45
2973.84	2974.04	2973.88
3248.75	3248.95	3248.79
3522.11	3522.32	3522.16
3793.90	3794.11	3793.94
4064.09	4064.31	4064.14
4332.65	4332.89	4332.73
4599.56	4599.80	4599.64
4864.78	4865.03	4864.86

Table 6. Exact and semiclassical energy levels of the one-dimensional hamiltonian.

$$H = \frac{1}{2}p_x^2 + \frac{1}{2}\lambda x^2 + b_1 x^4; \quad \lambda = 1, b_1 = -0.0015; \quad \text{dissociation energy} = 12102.5 \text{ cm}^{-1}.$$

Exact energy levels cm ⁻¹	Semiclassical energy levels cm ⁻¹
1203.29	1203.29
2198.35	2198.35
2611.77	2611.78
3193.39	3193.38
3600.78	3600.78
4020.23	4020.26
4188.40	4188.38
4589.70	4589.70
5003.16	5003.18
5183.39	5183.36
5428.70	5428.73
5578.54	5578.54
5985.96	5985.98
6178.35	6178.31
6405.53	6405.56
6567.30	6567.29
6837.15	6837.19
6968.63	6968.63
7173.27	7173.22
7382.19	7382.20
7556.01	7555.96
7807.87	7807.90
7951.15	7951.15
8168.15	8168.10
8245.59	8245.64
8358.65	8358.66
8544.56	8544.53
8778.52	8778.38
8933.52	8933.52
9163.02	9162.96
9210.16	9210.21
9334.91	9334.92
9533.03	9533.01
9654.02	9654.08
9748.58	9748.62
9915.74	9915.74
10157.83	10157.78
10174.46	10174.51
10310.96	10310.98
10521.42	10521.40
10612.43	10612.49
10718.58	10718.61
10897.80	10897.80
11062.43	11062.50
11138.46	11138.51
11152.63	11152.56
11286.82	11286.83

Table 7. Exact and semiclassical energy levels of the two-dimensional hamiltonian. $H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x^2 y^2$; $\lambda = 1$, $\mu = 0.5$, $b_1 = -0.003$; dissociation energy = 58817.9 cm⁻¹.

To investigate the accuracy of the energy levels we compare the 'exact' quantal energy levels supported by V_1 and V_2 with those obtained from the expressions (45) and (51).

Exact energy levels are found by diagonalizing the relevant hamiltonian matrices. For this purpose matrix elements of the hamiltonians with potentials V_1 and V_2 are calculated using harmonic oscillator wave functions as a basis.

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_2 , 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.

For each diagonalization a sufficient number of basis functions was chosen to ensure convergence of any tabulated energy levels to 0.01 cm^{-1} for the worst case.

Table 6 compares the lowest 18 exact energy levels of V_1 with the corresponding semiclassical energy levels obtained by the iteration procedure in equations (44), (45). A similar comparison is shown in table 7 for the lowest 47 energy levels of V_2 .

For the two-dimensional system the agreement between exact and semiclassical is better than for the one-dimensional system. This is a consequence of the fact that for V_2 the quantal perturbation series (52) and the classical perturbation series (50) are identical through first order in b_1 , whereas for V_1 there is a difference $3b_1/8$, between the quantal and classical first order energies. If we regard $3b_1/8$ as a first-order quantal correction to the semiclassical energy levels of V_1 and add it to (44) then the results are much improved (table 6).

7. CONCLUSIONS

The variational principle for invariant toroids and the E.B.K. quantization rule provide a useful range of methods for obtaining energy levels from potential surfaces.

The numerical iteration scheme of § 5 shows that toroids can be found for two and three degrees of freedom which are so accurate that it is difficult to determine any errors in them by stepwise integration of trajectories. The parametrization in terms of angle variables allows direct determination of action variables I_k , which is difficult using direct numerical integration of trajectories.

The analytic perturbation-variation method of § 6 is easier in practice than quantal perturbation theory for a given order of perturbation, as it does not require the extensive summation procedures of the latter. Unlike the analogous quantal case, the stationary principle provides a powerful practical technique for obtaining higher order energy levels from lower order invariant toroids. The evaluation of the energy function $E(\mathbf{I})$ and the substitution of the quantization conditions $I_k = (v_k + \frac{1}{2})\hbar$ enables large numbers of energy levels to be obtained together.

The method is not so accurate as quantal methods for low quantum numbers where the semiclassical expansion is not so good. It is straightforward to combine the method with low order quantal perturbation theory which may lead to improved results. Thus it is complementary to the usual quantal techniques.