

Vibrational quantization of polyatomic molecules II

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Received 21 May 1976, in final form 18 June 1976

Abstract. The semiclassical quantization method of Einstein, Brillouin and Keller is applied to some model Hamiltonians of two degrees of freedom which simulate non-separable molecular vibrations. A numerical scheme is based on the variation principle for invariant toroids and is used to obtain the regular energy spectrum over a wide range of energies. The scheme is rapid and effective, being about a factor $v_{\max}^2/(N^2 16^{N/2+1})$ faster than matrix diagonalization methods, where v_{\max} is a typical maximum vibrational quantum number and N is the number of degrees of freedom.

1. Introduction

The general theory of semiclassical quantization of the regular spectrum (Percival 1973) of bound systems of many degrees of freedom is due to Einstein (1917), Brillouin (1926) and Keller (1958) and to Maslov (1972). It is named EBK quantization and the field is reviewed by Percival (1977).

As described in a previous paper (Percival and Pomphrey 1976, to be referred to as I) a vibrational spectrum is determined from classical energy functions $E(\mathbf{I})$ of a vector action variable

$$\mathbf{I} = (I_1, I_2, \dots, I_N) \quad (1)$$

where N is the number of degrees of freedom. Each quantal state is labelled by vibrational quantum numbers

$$v_k \quad (k = 1, \dots, N)$$

and corresponds to an *invariant toroid* in classical phase space which has vector action variable \mathbf{I} with components

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

and approximate semiclassical energy given by the corresponding $E(\mathbf{I})$.

A prescription for obtaining invariant toroids is described in I. The practical determination of energy levels reduces to the determination of action variables of invariant toroids. This holds whether the Hamiltonian function of the system is separable or not. The problem is equivalent to the calculation of approximate constants of the motion in classical mechanics.

Eastes and Marcus (1974) and also Noid and Marcus (1975) use EBK quantization and stepwise numerical integration of trajectories to obtain invariant toroids and

Poincaré surfaces of section to derive action integrals. However numerical integration can be a lengthy procedure and it is difficult to obtain accurate integrals.

In I we gave a direct parametric representation of invariant toroids and used a variational principle (Percival 1974) to determine the energy function $E(\mathbf{I})$. Chapman *et al* (1976) also use EBK quantization and solve the Hamilton–Jacobi equation for the action function S by a numerical version of the iterative procedure given by Born (1960). The function S is the classical analogue of a unitary matrix in quantum theory.

The variational principle can be used to obtain a family of related methods of evaluating the energy function. In I we used it to derive a Taylor expansion in terms of a perturbation parameter. This is clearly limited by the radius of convergence of the expansion. We also used a numerical technique to obtain invariant toroids and checked them against direct numerical integration of trajectories, but we did not at the same time find the action variables, which is our present purpose.

We wish to obtain the energy levels $E(\mathbf{I})$ to a precision required by spectroscopy. The most efficient way of doing this is not by individual evaluation for specific energy levels, but by an evaluation of large numbers of close levels of the regular spectrum. For our examples we obtain $E(\mathbf{I})$ for the values of \mathbf{I} given by the quantization condition (2), but even this is not absolutely necessary provided $E(\mathbf{I})$ is obtained on a mesh of values of \mathbf{I} which can be adequately interpolated.

In §2 the variational principle for invariant toroids is described, and used to obtain the ‘angle Hamilton’s equations’.

The fundamental problem of small divisors which is familiar in celestial mechanics is discussed in relation to semiclassical iteration procedures in §3.

Section 4 presents an iteration scheme for the numerical determination of energy spectra, and §5 provides a comparison of estimated computation times with alternative quantal methods.

Finally in §6 we present the results of applying the numerical iteration scheme to two-dimensional model Hamiltonians, and it proves to be very effective for obtaining semiclassical energy levels. The models are similar in form to molecular potentials, for which the method should be effective.

2. Variational principle

We now restrict discussion to two degrees of freedom. Generalization is trivial, and is given with more details in I. Let

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

be points of the phase space and $H(\mathbf{q}, \mathbf{p})$ be the Hamiltonian function. A toroid Σ is defined parametrically by the periodic functional dependence of a point $\mathbf{X} = (\mathbf{q}, \mathbf{p})$ on the toroid on two angle variables θ_1, θ_2

$$\mathbf{X}_\Sigma(\theta_1, \theta_2) = (\mathbf{q}_\Sigma(\theta_1, \theta_2), \mathbf{p}_\Sigma(\theta_1, \theta_2)). \quad (4)$$

A normalized integral of a function $f(\theta_1, \theta_2)$ over the space of the action variables is defined by

$$\oint' d\tau_\theta f(\theta_1, \theta_2) = \frac{1}{(2\pi)^2} \int_{-\pi}^{\pi} d\theta_1 \int_{-\pi}^{\pi} d\theta_2 f(\theta_1, \theta_2). \quad (5)$$

The mean value of the energy on the toroid is

$$\langle E \rangle_{\Sigma} = \oint' d\tau_{\theta} H(\mathbf{q}_{\Sigma}(\theta_1, \theta_2), \mathbf{p}_{\Sigma}(\theta_1, \theta_2)) \quad (6)$$

and the mean of the k th action integral is

$$I_k(\Sigma) = \oint' d\tau_{\theta} \mathbf{p}_{\Sigma}(\theta_1, \theta_2) \cdot \partial \mathbf{q}_{\Sigma}(\theta_1, \theta_2) / \partial \theta_k. \quad (7)$$

An invariant toroid is one that is made up of classical trajectories for the system described by Hamiltonian H . The variational principle states that for invariant toroids, the mean energy is stationary subject to the action integrals remaining constant, that is

$$\Delta \Phi = \mathcal{O}(\Delta X)^2 \quad (8)$$

where

$$\Phi = \oint' d\tau_{\theta} [H(\mathbf{q}(\theta_1, \theta_2), \mathbf{p}(\theta_1, \theta_2)) - \omega_1 \mathbf{p} \cdot \partial \mathbf{q} / \partial \theta_1 - \omega_2 \mathbf{p} \cdot \partial \mathbf{q} / \partial \theta_2] \quad (9)$$

for arbitrary variations

$$\Delta X(\theta_1, \theta_2) = (\Delta \mathbf{q}(\theta_1, \theta_2), \Delta \mathbf{p}(\theta_1, \theta_2)). \quad (10)$$

Here the ω_k are Lagrange multipliers, but are later found to be the characteristic angular frequencies of the classical motion.

The variational principle for invariant toroids is the classical analogue of the variational principle for $(\psi, \hat{H}\psi)$, where ψ is a bound state of the system described by Hamiltonian operator \hat{H} (see I).

When the Hamiltonian function has the form

$$H = \frac{1}{2m} (p_1^2 + p_2^2) + V(q_1, q_2) \quad (11)$$

the action integrals can be written in terms of the coordinates

$$I_k \Leftarrow \sum_j G_{kj} \omega_j, \quad (12)$$

where G_{kj} is a generalized moment-of-inertia tensor given by (Percival 1974)

$$G_{kj} = m \oint' d\tau_{\theta} \frac{\partial \mathbf{q}}{\partial \theta_k} \cdot \frac{\partial \mathbf{q}}{\partial \theta_j}. \quad (13)$$

By the usual variational methods we obtain the 'angle Hamilton's equations'

$$\begin{aligned} \omega_1 \partial \mathbf{q} / \partial \theta_1 + \omega_2 \partial \mathbf{q} / \partial \theta_2 &= \partial H / \partial \mathbf{p} \\ \omega_1 \partial \mathbf{p} / \partial \theta_1 + \omega_2 \partial \mathbf{p} / \partial \theta_2 &= -\partial H / \partial \mathbf{q} \end{aligned} \quad (14)$$

where

$$\frac{\partial}{\partial \mathbf{q}} = \left(\frac{\partial}{\partial q_1}, \frac{\partial}{\partial q_2} \right), \quad \frac{\partial}{\partial \mathbf{p}} = \left(\frac{\partial}{\partial p_1}, \frac{\partial}{\partial p_2} \right). \quad (15)$$

These equations are partial differential equations for the toroid. They may be solved by a variety of iteration procedures, many of which require Fourier analysis with respect to the angle variables.

3. Principles of computation

When a system is separable, the invariant toroid is determined by the energy constants of the separated systems and the action integrals are the corresponding action integrals $(2\pi)^{-1} \oint p_k dq_k$ of the separated systems. In the case of the vibration of molecules the motion is approximately separable in the neighbourhood of equilibrium.

Separated motion of an unperturbed Hamiltonian H^0 is used as a starting point for the iterative procedures of this paper, but unlike the analytic perturbation-variation method of I these procedures are not power series expansions in a perturbation parameter.

In real molecules and others systems, the states of higher energy are very far from being separable; the classical motion can become irregular and the corresponding quantal spectrum is then also irregular. Invariant toroids do not exist and all methods then fail.

All iterative procedures run into the fundamental problem of small divisors or accidental degeneracy when characteristic frequencies approach values for which

$$v_1\omega_1 + v_2\omega_2 = 0 \quad (16)$$

(v_1 and v_2 integers, not both zero). In practice the problem is only serious when v_1 and v_2 are both fairly small in magnitude and the coupling strong. High v_1 or v_2 normally affect very small regions of phase space, and when these are smaller than $(2\pi\hbar)^2$ they have little influence on the problem of quantization and can be neglected.

For sufficiently strong coupling, the small v_1 and v_2 can produce irregular regions which occupy significant volumes of phase space. The problem of small divisors is fundamental because its presence may call into question the *existence* of invariant toroids of a given I_1 and I_2 , and not merely a computational difficulty (Percival 1973).

As the invariant toroids of the regular region approach the irregular region they become more and more convoluted. It is then difficult to represent them in any way but parametrically as in equation (4). Other methods, e.g. in terms of an action function $S(I_1, I_2, \theta_1^0, \theta_2^0)$ which generates the transformation from some fixed coordinate θ^0 to the action variable, run a strong risk of requiring many-valued functions, which are difficult to handle. The parametric representation in terms of angle variables (θ_1, θ_2) is always single valued.

The iteration procedure of §4 is a step-by-step solution for the energy levels $E(\mathbf{I}) = E(I_1, I_2)$ in which the invariant toroid for one value of (I_1, I_2) is used as a starting point for an iteration procedure for the next $(I_1 + \Delta I_1, I_2)$ or $(I_1, I_2 + \Delta I_2)$. In this work $\Delta I_k = \hbar$, but this is not essential. The variational principle (8) is used to ensure quadratic convergence.

4. Numerical scheme

We consider a Hamiltonian which has the form

$$H(\mathbf{r}, \mathbf{p}) = T(\mathbf{p}) + V(\mathbf{r}) \quad (17)$$

where

$$T(\mathbf{p}) = \frac{1}{2}(p_x^2 + p_y^2) \quad (18)$$

is the kinetic energy, and

$$V(\mathbf{r}) = \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 V^{\text{anh}}(x, y) \quad (19)$$

is the potential energy.

In I we showed that if the coordinates and momenta are expanded in Fourier series

$$\mathbf{r}(\theta_1, \theta_2) = \sum_{s_1, s_2} \mathbf{r}_{s_1, s_2} \exp[i(s_1 \theta_1 + s_2 \theta_2)] \quad (20)$$

$$\mathbf{p}(\theta_1, \theta_2) = \sum_{s_1, s_2} i(s_1 \omega_1 + s_2 \omega_2) \mathbf{r}_{s_1, s_2} \exp[i(s_1 \theta_1 + s_2 \theta_2)] \quad (21)$$

the following nonlinear equations result:

$$[\lambda - (s_1 \omega_1 + s_2 \omega_2)^2] x_{s_1, s_2} = F_{x_{s_1, s_2}}^{\text{anh}} \quad (22)$$

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

where $F_{s_1, s_2}^{\text{anh}}$ are the Fourier coefficients of the anharmonic force

$$\mathbf{F}^{\text{anh}}(\mathbf{r}) = -b_1 \nabla V^{\text{anh}}(\mathbf{r}). \quad (23)$$

Equations (22) can be used as a basis for a numerical iteration scheme to provide energy levels $E(I_1, I_2)$ of Hamiltonian H , which define an energy spectrum of H when

$$I_k = (v_k + \frac{1}{2})\hbar, \quad (k = 1, 2). \quad (24)$$

A toroid of the unperturbed Hamiltonian

$$H^0 = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) \quad (25)$$

is chosen as starting point for the procedure. Fourier series (20) and (21) with

$$x_{1,0} = x_{-1,0} = (I_1/2\lambda^{1/2})^{1/2}; x_{s_1, s_2} = 0 \quad (s_1, s_2) \neq (\pm 1, 0) \quad (26)$$

$$y_{0,1} = y_{0,-1} = (I_2/2\mu^{1/2})^{1/2}; y_{s_1, s_2} = 0 \quad (s_1, s_2) \neq (0, \pm 1)$$

and frequencies

$$\begin{aligned} \omega_1 &= \lambda^{1/2} \\ \omega_2 &= \mu^{1/2} \end{aligned} \quad (27)$$

define a toroid of H^0 labelled by action integrals I_1, I_2 . We wish to determine a toroid of H with the same values of I_1, I_2 .

A two-dimensional Fourier sum with coefficients (26) yields the corresponding doubly periodic functions $x(\theta_1, \theta_2), y(\theta_1, \theta_2)$ which can be used to obtain an approximate mean energy on the toroid through the equation

$$\langle E \rangle = \sum_{s_1, s_2} (s_1 \omega_1 + s_2 \omega_2)^2 (x_{s_1, s_2}^2 + y_{s_1, s_2}^2) + \oint d\tau_\theta V(x(\theta_1, \theta_2), y(\theta_1, \theta_2)). \quad (28)$$

The Fourier integral of the anharmonic force functions $\mathbf{F}^{\text{anh}}(x(\theta_1, \theta_2), y(\theta_1, \theta_2))$ yields corresponding Fourier coefficients $F_{s_1, s_2}^{\text{anh}}$ which are required to obtain a more accurate representation of the toroid: equations (22) with $(s_1, s_2) = (1, 0), (s_1, s_2) = (0, 1)$ are used to obtain corrected frequencies ω_1, ω_2 and also to obtain the corrected Fourier coefficients of position

$$\begin{aligned} x_{s_1, s_2} & \quad (s_1, s_2) \neq (\pm 1, 0) \\ y_{s_1, s_2} & \quad (s_1, s_2) \neq (0, \pm 1). \end{aligned} \quad (29)$$

$x_{\pm 1,0}$ and $y_{0,\pm 1}$ are obtained at each stage of the iteration by inverting equations (12) and (13) (see appendix).

The description of one cycle of the iteration for an energy level $E(I_1, I_2)$, with chosen I_1, I_2 is now complete. Figure 1 shows a flow chart which illustrates how this cycle is used to determine the energy spectrum of H .

The invariant toroid for one value of I is used as a starting point for the iteration for the energy level $E(I + \Delta I)$, and ΔI may be chosen in a variety of ways. Figure 2 shows two possible ways in which a grid of values I_1, I_2 can be covered. The lines joining adjacent points of the grid indicate the order in which the energy levels $E(I)$ are to be determined; both methods were used in practice.

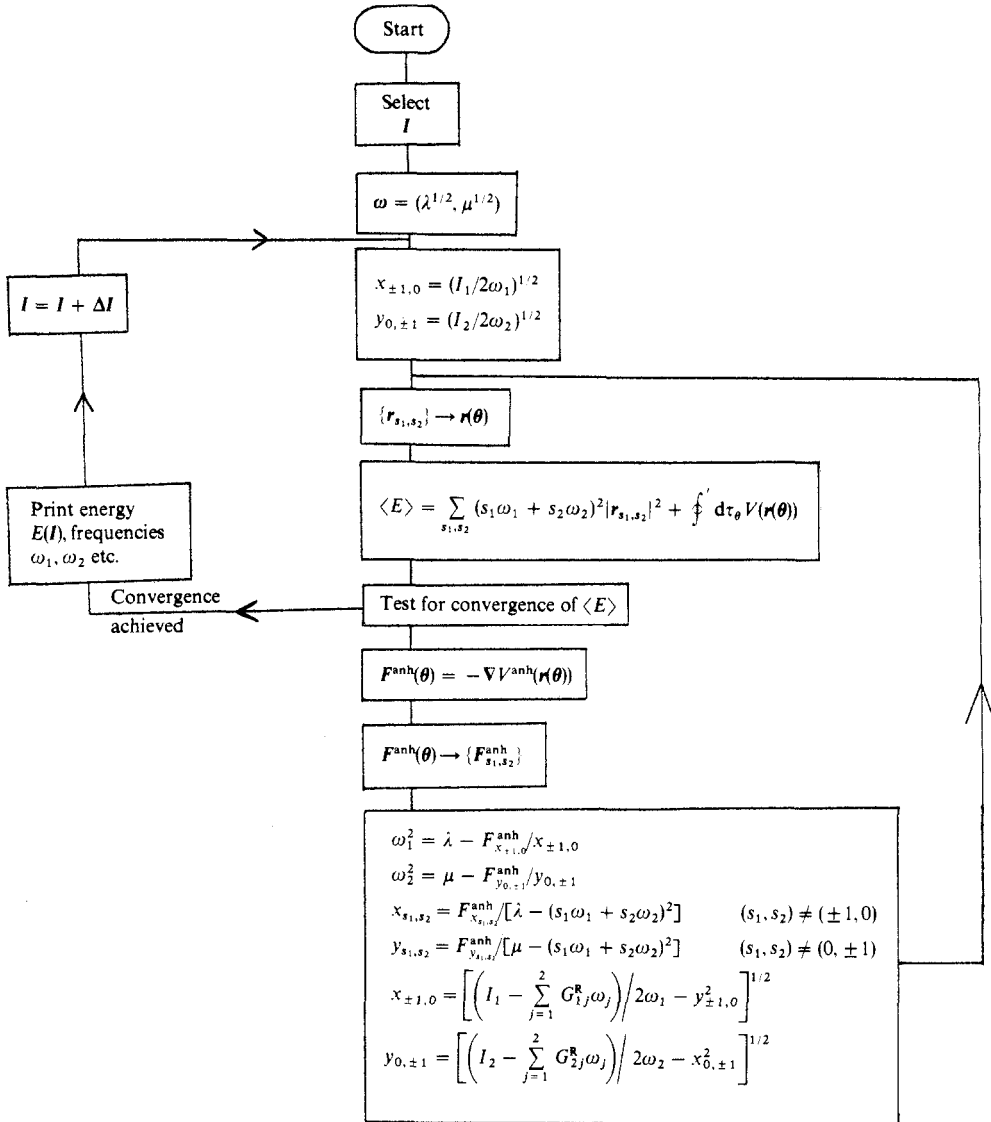


Figure 1. Flow chart for iteration scheme for energy spectrum of $H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 V^{\text{anh}}(x, y)$.

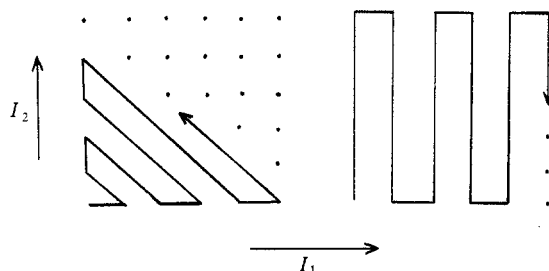


Figure 2. Two possible schemes for spanning the I space.

At any stage of the iterations for a given energy level the ratio ω_1/ω_2 of the approximate frequencies will depend on which toroid has been chosen as starting point, or, in other words, on the choice of ΔI . If the frequencies satisfy low-order resonance conditions of the form (16), then progress will be halted by the existence of zero denominators. In this case it is frequently possible to alter the choice of ΔI so that zero denominators are avoided. An exceptional case where this procedure cannot be implemented occurs when the frequencies on the *invariant* toroid are accidentally degenerate. Further improvements of the method are in hand.

5. Computational method

For two degrees of freedom each doubly periodic function $f(\theta_1, \theta_2)$ is approximated by a finite double Fourier sum of M^2 terms and the functions f are tabulated on an $M \times M$ mesh of equally spaced points spanning the space of the angle variables

$$-\pi < \theta_1 \leq \pi, \quad -\pi < \theta_2 \leq \pi.$$

The iterations for a particular energy level can be considered to be successfully completed when the difference between successive values of the mean energy is less than some tolerable value Tol .

The number of arithmetic operations required to perform a two-dimensional fast Fourier transform of an $M \times M$ array of elements depends on $2M^2 \log_2 M$. Since each cycle of the iteration described in §4 employs four such transforms, the computational time required to determine an energy level $E(I_1, I_2)$ to accuracy Tol depends on $8KM^2 \log_2 M$ where K is the number of iterations. It is important to realize that both K and M are normally insensitive to I_1 and I_2 (§6). In contrast, the corresponding time per level required by standard quantal methods such as matrix diagonalization is proportional to L^2 , where L is the number of basis wavefunctions. Clearly the effectiveness of the semiclassical method gains rapidly over quantal methods as I_1 and I_2 are increased. For the calculation of vibrational levels of molecules with N degrees of freedom, the semiclassical iteration procedure is expected to be about a factor $v_{\max}^{2N}/(N^2 16^{N/2+1})$ faster than matrix diagonalization methods, where v_{\max} is a typical maximum vibrational quantum number. This estimate has been obtained assuming that, for the diagonalization method, the number of basis functions required for the adequate representation of a vibrational energy level with vibrational quantum number v_{\max} is proportional to $4^{N/3} v_{\max}^N$. This is clearly an optimistic estimate. Finally it is important to note that the semiclassical iteration method does not run into the severe computer storage problems of quantal matrix methods, where very large bases are needed.

Table 1. Semiclassical eigenvalues of the non-separable Hamiltonian

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

The parameter values are: $\lambda = 0.49$, $\mu = 1.69$, $b_2 = -b_1$, $Tol = 0.0001$, $M \leq 16$.

| b_1 | Escape energy D | Semiclassical | | | Semiclassical | | | Semiclassical | | |
|-------|-------------------|---------------|---------|---------|---------------|---------|---------|---------------|---------|---------|
| | | Chapman† | Present | Quantal | Chapman† | Present | Quantal | Chapman† | Present | Quantal |
| 0 | — | 1.0 | 1.0 | 1.0 | 1.7 | 1.7 | 1.7 | 2.3 | 2.3 | 2.3 |
| -0.06 | 168.1084 | 0.9987 | 0.9987 | 0.9988 | 1.6970 | 1.6970 | 1.6970 | 2.2932 | 2.2932 | 2.2932 |
| -0.08 | 53.1906 | 0.9975 | 0.9975 | 0.9975 | 1.6933 | 1.6933 | 1.6933 | 2.2870 | 2.2870 | 2.2870 |
| -0.10 | 21.7869 | 0.9955 | 0.9955 | 0.9955 | 1.6870 | 1.6870 | 1.6870 | 2.2782 | 2.2782 | 2.2781 |
| -0.12 | 10.5068 | 0.9927 | 0.9927 | 0.9926 | 1.6770 | 1.6770 | 1.6769 | 2.2661 | 2.2661 | 2.2658 |
| -0.14 | 5.6713 | 0.9889 | 0.9889 | 0.9884 | 1.6617 | 1.6617 | 1.6612 | 2.2496 | 2.2498 | 2.2490 |
| -0.16 | 3.3244 | 0.9836 | 0.9836 | 0.9826 | 1.6382 | 1.6382 | 1.6370 | 2.2268 | 2.2266 | 2.2257 |

†See Chapman *et al* (1976).

6. Results

The non-separable two-dimensional quadratic Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x^2 y^2 \quad (30)$$

has been considered in detail in I, where a perturbation variation method was used to obtain an expression for the energy function $E(I_1, I_2)$ as an expansion in powers of b_1 . The problem of barrier penetration can be ignored, for the same reason as in the theory of the Stark effect for weak fields.

The numerical iteration scheme described in this paper has also been applied to Hamiltonian (30) with the following parameter values: $\lambda = 1.0$, $\mu = 0.5$, $b_1 = -0.003$ and $\hbar = 1$. The results reproduce with a maximum deviation of 0.04 cm^{-1} those obtained by the authors in I using the perturbation variation method.

$M = 8$ was sufficient to achieve convergence of each of the lowest 45 energy levels to within an accuracy $Tol = 0.01 \text{ cm}^{-1}$. The number of iterations required for convergence of each energy level was never greater than three. Agreement between semiclassical and quantal results is very good.

Much attention has recently been paid to the non-separable cubic Hamiltonian

$$H = \frac{1}{2}(p_x^2 + p_y^2) + \frac{1}{2}(\lambda x^2 + \mu y^2) + b_1 x(y^2 + b_2 x^2). \quad (31)$$

Eastes and Marcus (1974) and also Noid and Marcus (1975) were the first workers to apply a semiclassical technique to the problem of determining the energy levels of multi-dimensional non-separable systems and they concentrated their efforts on Hamiltonian (31). Chapman *et al* (1976) have also been able to determine semiclassical energy levels of (31) using a method which is due to Born (1960). For fixed λ and μ , these authors calculate energy levels for a range of values of b_1 and b_2 which test the semiclassical method under conditions of strong as well as weak perturbations.

Table 1 presents the results of applying the numerical iteration procedure of this paper to the Hamiltonian (31). 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 agree well with those obtained by Chapman *et al*.

Acknowledgments

We thank the SRC for a research grant.

Appendix

To obtain corrected coefficients of position $x_{\pm 1,0}$, $y_{0,\pm 1}$, equations (12) and (13) are inverted. Writing

$$I_k = \sum_{j=1}^2 (G_{kj}^F + G_{kj}^R)\omega_j, \quad k = 1, 2 \quad (A.1)$$

where

$$\begin{aligned} G_{11}^F &= 2(x_{\pm 1,0}^2 + y_{\pm 1,0}^2), & G_{11}^R &= \sum_{s_1, s_2 \neq \pm 1, 0} s_{11}^2 (x_{s_1, s_2}^2 + y_{s_1, s_2}^2) \\ G_{22}^F &= 2(x_{0, \pm 1}^2 + y_{0, \pm 1}^2), & G_{22}^R &= \sum_{s_1, s_2 \neq 0, \pm 1} s_{22}^2 (x_{s_1, s_2}^2 + y_{s_1, s_2}^2) \end{aligned} \quad (A.2)$$

and

$$G_{12}^F + G_{12}^R = G_{21}^F + G_{21}^R = \sum_{s_1, s_2} s_1 s_2 (x_{s_1, s_2}^2 + y_{s_1, s_2}^2).$$

The corrected fundamental coefficients of position are then given by

$$\begin{aligned} x_{\pm 1, 0} &= \left[\left(I_1 - \sum_{j=1}^2 G_{1j}^R \omega_j \right) / \left(2\omega_1 - y_{\pm 1, 0}^2 \right) \right]^{1/2} \\ y_{0, \pm 1} &= \left[\left(I_2 - \sum_{j=1}^2 G_{2j}^R \omega_j \right) / \left(2\omega_2 - x_{0, \pm 1}^2 \right) \right]^{1/2}. \end{aligned} \tag{A.3}$$

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