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Semiclassical analysis of Hénon-Heiles coupled oscillators: quasi-periodic and chaotic quantum behavior and the resonance model of unimolecular decay

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The quantum mechanics of the Hénon-Heiles potential is analyzed using an adiabatic representation in polar coordinates and exploiting the asymptotic separability of the radius. The procedure allows us to establish a correlation between quasiperiodic and chaotic classical behavior, and regular or irregular quantum modes: It is found that irregularity can be attributed to nonadiabatic effects at the potential ridge. The resonance widths for this prototypic system of coupled oscillators are studied with reference to the lifetime in the quantum theory of unimolecular decay. The near separability of the radius of the polar coordinate representation is exploited for discussing energy dependence and symmetry effects on the widths. The relevance of this analysis for the characterization of quantum mechanical behavior near an elliptic umbilic catastrophe point is also briefly considered.

Key words: Hénon-Heiles potential — Coupled oscillators — Adiabatic representation — Chaotic quantum modes — Elliptic umbilic catastrophes — Resonance widths

1. Introduction

Basic to several recent investigations of nonseparability in celestial mechanics is a potential known as Hénon-Heiles' [1], which is obtained by adding a cubic term to the isotropic bidimensional oscillator:

$$V(x, y, \lambda) = \tfrac{1}{2}(x^2+y^2) + \lambda\left(xy^2 - \frac{x^3}{3}\right), \qquad (1)$$

the strength of coupling being measured by the parameter λ. Studies of bifurcation for the propped cantilever [2] and general Hamiltonian dynamics [3] use similar potential functions; in chemical physics, this potential is of interest for intramolecular vibrational relaxation [4]. For the classical Hénon-Heiles' oscillator, quasiperiodic and chaotic trajectories have been characterized. Correspondingly, it is pointed out in this paper that quantum mechanical states can be classified as regular or irregular [5], the origin for irregularity being associated with a nonadiabatic coupling localized along ridges in the potential [6].

Features of the potential (1) and of the present analysis are sketched in Fig. 1.

The adiabatic analysis, as presented in Sect. 2 [6], is most transparent when the potential is written in polar [7] coordinates,

$$V(\rho,\theta)=\tfrac{1}{2}\rho^2-\frac{\lambda\rho^3\cos 3\theta}{3}, \tag{2}$$

where $x=\rho\cos\theta$, $y=\rho\sin\theta$ have been substituted in (1). This potential has C_{3v} symmetry, with valley bottoms for $\theta=(0, 2\pi/3, 4\pi/3)$ and ridges for $\theta=(\pi/3, \pi, 5\pi/3)$ [8]. Valley bottoms attain a maximum value of $(6\lambda^2)^{-1}$ high when $\rho=\lambda^{-1}$ (the saddles of the surface), and then go to minus infinity: all the states quantum mechanically supported by this potential energy surface are actually metastable. Following Miller [9, 10], the energy positions and widths of these

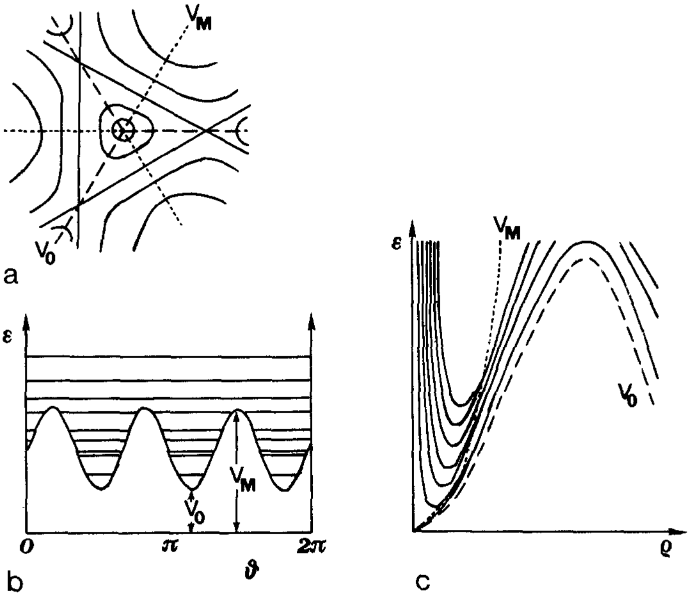


Fig. 1. **a** Schematic diagram of equipotential curves for the Hénon-Heiles model of anharmonically coupled oscillators (Eqs. (1), (2)); **b** energy levels supported by a threefold pendular type potential as obtained from the Hénon-Heiles potential at fixed ρ. The minimum V_0 (valley bottom) and the maximum V_M (ridge) of the ρ-fixed potential are indicated; **c** V_M and V_0 as a function of ρ, together with typical behaviour of adiabatic energy levels ε

quantum mechanical resonances have been considered as a model for unimolecular dissociation reactions [9–11]. The semiclassical analysis based on short wave asymptotic separability [6] still needs to be solved for adiabatic bound states at fixed ρ. As shown in Sect. 3 this problem is essentially that of the quantum mechanics of the pendulum [12], described by Mathieu eigenvalues and functions; symmetry classifications and general qualitative features follow easily from this analysis. Its application to the characterization of resonance widths is considered in Sect. 4, where we use the approach recently introduced for similar problems in unimolecular reaction theory [13]. In an Appendix we conclude with some remarks on the canonical nature of this problem and the implications from a catastrophe theory viewpoint.

2. Semiclassical analysis in the adiabatic representation

2.1. Asymptotic separability and its local breakdown

Because of the masses and the interactions involved, molecular behavior is typically a problem for semiclassical mechanics: quantum effects are too important to be neglected altogether, but Planck's constant is definitely so small a parameter that appropriate asymptotic techniques can be exploited effectively. The paradigmatic example is the WKB (Wentzel, Kramers, Brillouin) approach; it is useful both for bound states and for scattering [14] whenever the problem is essentially one-dimensional, and in the following discussion we will base many of our considerations on it.

The extension of the asymptotic approach [15] to multidimensional nonseparable systems is not so straightforward; EBK (Einstein, Brillouin, Keller) quantization acts only on classical quasiperiodic trajectories, thus yielding only part of the spectrum, and cannot be generalized to scattering states. Among the techniques developed for dealing explicitly with inelastic scattering and reactions, a generalization of the Born–Oppenheimer separation of nuclear and electronic motion has recently proved to be very successful in atomic [16] and molecular [17] physics. It involves the search for a nearly separable variable, in terms of which the time independent Schrödinger equation reduces to an infinite set of coupled second-order ordinary differential equations. As will be shown below, besides offering an effective computational scheme, the procedure may be implemented semiclassically, and each step is amenable to the qualitative interpretation that is needed for deepening our insight into complicated quantum systems.

Regular, quasiperiodic behavior of a quantum system is definitely associated with at least some degree of separability of the equations of motion. (How the converse, i.e., "chaos" whatever its definition may be, can be associated with nonseparability, is a matter of current research [18]). Separability, on the other hand, is always a manifestation of some symmetry. This, in quantum mechanics, corresponds to the existence of operators commuting with the Hamiltonian, and leads to the possibility of defining good quantum numbers. Although for intrinsically nonseparable problems separation cannot be carried out exactly (globally), it is nonetheless possible to find important examples where quasiseparability (approximately commuting operators, nearly good quantum numbers) can be obtained. In the description of diatomic molecules, for example, electronic, vibrational and rotational modes are progressively considered separately following a well established hierarchy, and this allows one to arrange modes according to characteristic frequencies. The underlying idea is that if a mode is much slower than others, it can be considered as frozen while studying the fast ones. Thus, in the familiar Born-Oppenheimer separation, internuclear distances are slow coordinates with respect to electron-nucleus and electron-electron ones. The whole of quantum chemistry capitalizes on this idea.

A key observation for fruitful generalization is that, to achieve approximate separation, one employs, more or less rigorously, asymptotic expansions with respect to some parameters (mass ratios, frequency ratios). In the present investigations, we start from the consideration that, for problems of definite chemical and physical interest, it is often possible to find some representation which allows us to obtain an approximate separation (at least locally) by expansions which are asymptotic in Planck's constant, treated as a small parameter. This is a natural choice, since it corresponds to what is commonly understood as the short wave, or semiclassical, regime. Although these approximately separated representations will fail somewhere, it is surmised [6] that the localization of failure may lead to the identification of a source of irregular behavior for quantum modes, suggesting therefore that the search for special asymptotic techniques for dealing with local nonseparability is particularly promising.

2.2. Adiabatic and diabatic representations

In general, within the framework of time independent nonrelativistic quantum mechanics, a Born-Oppenheimer type of separation can be attempted by introducing a suitable coordinate system. Suppose the problem to be N-dimensional: in typical applications [17], one variable ρ is defined, in most cases as a radius of the N-hypersphere, and the problem is parametrized by $n = N-1$ angles, collectively indicated by $\mathbf{\Omega}_n$. The Schrodinger equation can then be transformed into a coupled set of ordinary differential equations with the diagonal elements being $\varepsilon_\nu(\rho)$, the spectrum of an $(N-1)$ dimensional problem parametrically depending on ρ, with corresponding wavefunctions $\phi_\nu^a(\rho, \mathbf{\Omega}_n)$.

When the total wavefunction is expanded in an adiabatic basis set

$$\mathbf{\Psi}(\rho, \mathbf{\Omega}_n) = \rho^{-n/2}\mathbf{\Phi}^a(\rho, \mathbf{\Omega}_n)\mathbf{F}^a(\rho), \tag{13}$$

the hyperradial adiabatic functions $\mathbf{F}^a$ are to be found as the solutions, with proper boundary conditions, of the infinite set of coupled linear differential equations [19]

$$\left\{-\frac{\hbar^2}{2\mu}\left[\mathbf{1}\frac{d}{d\rho}+\mathbf{P}(\rho)\right]^2+\boldsymbol{\varepsilon}(\rho)-E\mathbf{1}\right\}\mathbf{F}^a(\rho)=0. \tag{4}$$

Here, the matrix of adiabatic eigenfunctions, $\mathbf{\Phi}^a(\rho, \mathbf{\Omega}_n)$, and the diagonal matrix of adiabatic potential energy curves, $\varepsilon_\nu(p)$, are solutions of the eigenvalue problem

$$\left\{-\frac{\hbar^2}{2\mu\rho^2}\left[\mathbf{\Lambda}^2-\frac{n^2}{4}+\frac{n}{2}\right]+V(\rho, \mathbf{\Omega}_n)-\boldsymbol{\varepsilon}(\rho)\right\}\mathbf{\Phi}^a(\rho, \mathbf{\Omega}_n)=0, \tag{5}$$

where the operator Λ^2 is the angular part of the Laplacian of the $(n+1)$-dimensional space, and $V(\rho, \mathbf{\Omega}_n)$ is the interaction potential. The infinite sets are meant to be solved after proper truncation. The mass parameter μ, which appears in Eq. (4), depends on the definition of the hyperradius ρ.

The adiabatic approximation consists of neglecting all coupling in Eq. (4), i.e. in neglecting the elements of the antisymmetric matrix $\boldsymbol{P}(\rho)$,

$$P_{\nu\nu'} = \left\langle \Phi^a_\nu \left| \frac{\partial}{\partial\rho} \Phi^a_{\nu'} \right.\right\rangle = (\varepsilon_\nu - \varepsilon_{\nu'})^{-1} \left\langle \Phi^a_\nu \left| \frac{\partial V}{\partial\rho} \Phi^a_{\nu'} \right.\right\rangle = -P_{\nu'\nu}, \tag{6}$$

the brackets denoting integration over hyperangles $\mathbf{\Omega}_n$, and use has been made of a form of the so called the Hellmann-Feynman theorem. Some authors [20] add to ε_ν the diagonal terms of a matrix $\boldsymbol{Q}(\rho)$ given by $\boldsymbol{Q} = -\boldsymbol{P}^2 + d\boldsymbol{P}/d\rho$. The present scheme would then be referred to as the Born-Oppenheimer approximation. Actually, it can be shown by variational theory that for ground states this approximation gives a lower limit, while the Q-corrected one gives an upper limit; however, the latter approximation becomes ill-behaved when nonadiabatic coupling is important. A scheme for further corrections to the adiabatic approximation has been developed [19].

We note that diabatic representations [12] correspond to alternative expansions to those in Eq. (3).

$$\boldsymbol{\Psi}(\rho, \mathbf{\Omega}_n) = \rho^{-n/2} \boldsymbol{\Phi}^d(\mathbf{\Omega}_n) \boldsymbol{F}^d(\rho) \tag{7}$$

By comparison with Eq. (3), Eq. (7) implies the definition of an orthogonal matrix $\boldsymbol{T}(\rho)$,

$$\boldsymbol{\Phi}^a(\rho, \mathbf{\Omega}_n) = \Phi^d(\mathbf{\Omega}_n)\boldsymbol{T}(\rho) \quad \text{and} \quad \boldsymbol{F}^d(\rho) = \boldsymbol{T}(\rho)\boldsymbol{F}^a(\rho),$$

which can be obtained once Eq. (5) has been solved, by requiring that the orthogonal matrix $\boldsymbol{T}(\rho)$ satisfy the system

$$\boldsymbol{P}(\rho) = \tilde{T}(\rho) \frac{d}{d\rho} \boldsymbol{T}(\rho). \tag{8}$$

As a result, first derivatives disappear from Eq. (4), which becomes

$$\left\{ -\frac{\hbar^2}{2\mu} \left[\frac{d^2}{d\rho^2} + E \right] \mathbf{1} + \boldsymbol{V}(\rho) \right\} \boldsymbol{F}^d(\rho) = 0, \tag{9}$$

the coupling being transferred from the kinetic term in Eq. (4) to the potential, which now is a nondiagonal diabatic matrix related to $\boldsymbol{\varepsilon}(\rho)$ by

$$\boldsymbol{V}(\rho) = \boldsymbol{T}(\rho)\boldsymbol{\varepsilon}(\rho)\tilde{\boldsymbol{T}}(\rho). \tag{10}$$

This prescription is not unique, since any ρ-independent rotation of $\boldsymbol{T}$ is also a solution: boundary conditions have to be imposed on Eq. (8). A particular advantage of our choice of the ρ coordinate is that a convenient analytical diabatic expansion basis may be given by the eigenfunctions of Λ^2 in Eq. (5), i.e. by the (hyperspherical) harmonics [17].

In the following, we will exploit properties of the adiabatic formulation. At a given total energy E, one has to introduce the proper (scattering or bound states) boundary conditions and solve for the unknown channel functions $\boldsymbol{F}^a(\rho)$. The $\boldsymbol{\varepsilon}$ and $\boldsymbol{P}$ matrices, which are obtained by solving an $N-1$ dimensional problem, are in principle of infinite dimension. The success of the procedure from the point of view of its use in practical calculations is determined by its rate of convergence upon truncation.

The above manipulation of the Schrödinger equation is particularly useful for a discussion of properties of systems from the point of view of asymptotic methods. It is immediately apparent that whenever elements of $\boldsymbol{P}$ are small, since $\hbar^2/2\mu$ is a small parameter in molecular dynamics and chemical kinetics, Eq. (4) adiabatically decouples into one-dimensional Schrödinger problems for the effective potentials $\varepsilon_\nu(\rho)$. In turn, these one-dimensional equations can be analyzed by the Liouville-Green WKB technique. This requires special care whenever $\varepsilon_\nu(\rho)=E$ (turning points), but may be effectively solved by the method of comparison equations (see Appendix). Therefore a proper choice of coordinates may lead to wide regions of ρ space where this decoupling is very effective; in these cases it may be straightforward to compute bound or resonance states and scattering properties semiclassically.

When this adiabatic decoupling is effective, wave functions are given by a single term of expansion (3), and approximate quantum numbers can be assigned. However strictly the class of regular, quasiperiodic modes are defined in quantum mechanics, these states definitely appear to belong to it! As will be illustrated below, the success of the procedure critically depends on how appropriate the definition of the ρ coordinate is, with ρ being chosen to localize any breakdown of approximate separability as much as possible. This breakdown is measured by the $\boldsymbol{P}$ matrix, and therefore a study of its analytical structure is an important step in the present program. In fact, Eq. (4) shows that around those poles of the $\boldsymbol{P}$ matrix elements that are sufficiently close to the real ρ axis, their neglect is not warranted however small $\hbar^2/2\mu$ becomes. In the following, therefore, we will sketch examples where these features of $\boldsymbol{P}$ matrix have been characterized. Around these features adiabatic conditions fail, and several terms of comparable magnitude may contribute to Eq. (3), leading to departure from regular behavior.

3. Regular and irregular quantum modes of Hénon–Heiles coupled oscillators

3.1. *Reduction to Mathieu equation*

The quantum mechanics for a particle in a Hénon–Heiles potential $V(\rho,\theta)$ (Eq. 2) is described by the Schrödinger equation, which in proper units [4] reads, at the energy E,

$$\left\{-\frac{1}{2}\left(\frac{\partial^2}{\partial\rho^2}+\frac{1}{\rho}\frac{\partial}{\partial\rho}+\frac{1}{\rho^2}\frac{\partial^2}{\partial\theta^2}\right)+V(\rho,\theta)\right\}\Psi(\rho,\theta)=E\Psi(\rho,\theta). \tag{11}$$

The adiabatic expansion of Eq. (3) is now

$$\Psi(\rho,\theta)=\rho^{-1/2}\sum_\nu \phi_\nu(\rho,\theta)F_\nu^a(\rho), \tag{12}$$

where the functions $\phi_\nu(\rho, \theta)$ are eigensolutions at *fixed* ρ values to the equation

$$\left\{-\frac{1}{2}\left(\frac{1}{\rho^2}\frac{\partial^2}{\partial\theta^2}\right)+V(\rho, \theta)\right\}\phi_\nu(\rho, \theta)=\varepsilon_\nu(\rho)\phi_\nu(\rho, \theta). \tag{13}$$

The choice of the polar coordinate system for this problem is particularly convenient since the cyclic boundary conditions mean that Eq. (13) yields a discrete spectrum. This advantage also encourages the use of polar coordinates for spaces of higher dimension [17].

The eigenvalue equation, Eq. (13), is essentially a Mathieu equation, which in quantum mechanics describes the properties of a pendular motion. Therefore we will summarize its properties in the next section, surmising that the quantum pendulum is the prototypic physical model for mode transitions, and that the Mathieu equation, its eigenvalues, and its eigenfunctions, provide the appropriate mathematical apparatus for the description of mode transitions.

3.2. Transition between modes: semiclassical analysis of the quantum pendulum

Nonadiabatic effects are often localized where the actual character of a system changes drastically. So, for example, when the interaction between two atoms is considered as a function of the internuclear distance R, it is found that the transition between the typical behavior of separated atoms and that of a diatomic molecule is often localized around sharp maxima in elements of a $\boldsymbol{P}(R)$ matrix [19]. These maxima correspond to poles near the real R axis in a proper analytic continuation of $\boldsymbol{P}(R)$, and mark the breakdown of the Born-Oppenheimer separation.

Several examples can be put forward in order to show that transitions between modes, due to a local breakdown of adiabaticity, typically take place at well defined characteristic features of the potential. For problems involving more than two bodies, several investigations have identified the hyperradial variable ρ as a good candidate for near separability [16, 17]. Low values of ρ correspond to closeness of all particles, and the various possible rearrangement channels correspond to large ρ. Consider the simplified situation where three particles are constrained to be on a line. A rearrangement process, such as a chemical reaction, can be described [21] in a time independent picture as the transition between two types of modes, with the transition corresponding to an intermediate complex (transition state) which may dissociate into channels corresponding to reactants and products; the transition can be described adiabatically, nonadiabaticity being important only along a line in the potential energy surface (the ridge) which separates the valleys of reactants and products. Implementing these ideas semiclassically, it has been possible to obtain not only qualitative descriptions, but also quantitative results for resonance positions and widths, and for interference effects in the probability for reactive collisions. A classical study of these problems [22] points to a connection between chaotic behavior and temporary trapping in the transition state; again, a connection between local nonseparability and irregular modes is emerging.

As stressed above, the basic physics and the related mathematics associated with mode transitions are illustrated by the pendulum, whose classical mechanics is described in many textbooks and reviews [23]. The two modes are designated vibrating or librating, and rotating or precessing at energies respectively lower and higher than the maximum in the potential V_M. In the context of recent investigations of highly excited molecules, the two modes would correspond for example to normal and local vibrations, respectively. The two modes are sharply separated by a trajectory (the separatrix) that has an energy corresponding to the maximum in the potential (the ridge in our applications). As is often the case, the transition between modes is smoother in quantum mechanics [24].

Since (see Sect. 2.1) the pendulum problem figures in our treatment of Hénon-Heiles potential, we sketch some of its features.

Mathematically, the classical problem is completely soluble in terms of Jacobian elliptic functions and the quantum problem in terms of Mathieu, or elliptical cylinder, functions. The limiting behavior of quantum solutions for the two modes are very well known, and the literature contains extensive discussions of this behaviour. Both can be handled by perturbation techniques [25]; however these fail around the ridge, where a connection problem arises. Therefore, a discussion of the transition regime is of specific interest, and can be carried out by the simple uniform asymptotic technique sketched in [5].

The Schrödinger equation for the physical pendulum [23],

$$\left[-\frac{\hbar^2}{2ml^2}\frac{d^2}{d\phi^2}+V_M\cos\phi\right]\Psi_\nu(\phi)=\varepsilon_\nu\Psi_\nu(\phi) \tag{14}$$

(where m is the mass and l the length, and ε_ν the energy for the state Ψ_ν), is transformed into the standard Mathieu equation,

$$\frac{d^2}{d\alpha^2}Y_\nu(\alpha)+(\Lambda_\nu-2q\cos 2\alpha)Y_\nu(\alpha)=0, \tag{15}$$

by defining a new angle $\alpha=\phi/2$, the parameter $q=4ml^2V_M/\hbar^2$ and the eigenvalue $\Lambda_\nu=8ml^2\varepsilon_\nu/\hbar^2$.

Eigenvalues and eigenfunctions for this equation can be generated by using expansions in Fourier series (Hill's method) [26], being the complex exponential harmonics on a circle [17]:

$$Y_\nu(\alpha)=\sum_{r=-\infty}^{\infty}t_{2r,\nu}\exp\left[i(\beta+2r)\alpha\right] \tag{16}$$

(where β depends on boundary conditions dictated by symmetry—see below). Insertion of this expansion in Eq. (15) leads to a secular equation, giving Λ_ν as eigenvalues, and the coefficients $t_{2r,\nu}$ as elements of eigenvectors. The present secular problem has been efficiently solved by Jacobi diagonalization.

For the pendulum, the boundary conditions on Eq. (15) require the solutions in α to have π as a period, and one obtains (as a function of q) even and odd eigenvalues, usually denoted a_{2n} and b_{2n} respectively. Equation (15), as the simplest case of a Hill equation, may represent a zero-order approach to problems where a potential is expanded in a Fourier series. In general, therefore, other periodic boundary conditions are of interest. A Floquet type of analysis [26] shows that for N-fold symmetric potentials (where N is even), solutions with period 2π are also acceptable. Corresponding eigenvalues are denoted a_{2n+1} and b_{2n+1} for the even and odd cases respectively. In the language of group theory, only states with the same periodicity and parity will belong to the same irreducible representation of the symmetry group of the potential.

For general N, doubly degenerate solutions also appear, and their eigenvalues are labelled by $2n+\beta$, where β is a rational fraction less than 2: $\beta=2K/N$, and $K=1,\ldots,-1$. They induce irreducible representations of type ε. It is convenient to extend the definition of K (and β) to the nondegenerate cases, corresponding to $K=0$ (and $\beta=0$) for $2n$ states (π periodicity) and $K=N/2$ (and $\beta=1$) for $2n+1$ states (2π periodicity).

The behavior of the eigenvalues as a function of q, well documented in the literature [27, 28], is very clearly exhibited by a semiclassical analysis [12].

Following [29], it is possible to obtain, by an extended WKB procedure, a quantization rule; this has been studied in detail recently [12]. It has been found that the approach is useful not only for the approximate computation of eigenvalues, but also for describing most qualitative features of the transitions between modes as a function of q—the behavior of the allowed and forbidden regions for the eigenvalues (see Fig. 2) illustrates these features. The next section focuses on the localization of mode transitions in particular.

*3.3. The **P** matrix and the ridge effect*

As shown in Fig. 2 and in several figures in books that describe the properties of Mathieu functions [26-28], the variation of the eigenvalues as a function of q show an abrupt change in character as they go through a line corresponding to $2q$, which is classically the locus of separatrix trajectories. This is perhaps the simplest manifestation of the ridge effect, and, according to the nomenclature now well established in atomic physics [16, 17] and in chemical reaction theory [21, 30-33], $2q$ is identified as the ridge line (and $-2q$ is the valley bottom line) for the physical applications of these results.

In typical problems, q is the slowly varying variable in an adiabatic treatment, but the fast variables fail to be so at the ridge. (For the Hénon-Heiles potential, q is related to a slow varying radial variable ρ [see Sect. 3.4]). Nonadiabaticity, i.e. the possibility of transition between states as q varies, is measured by the matrix $\boldsymbol{P}$ (Eq. 6) which explicitly has elements

$$P_{\nu\nu'}(q)=\int_0^{2\pi} Y_\nu(\alpha,q)\frac{d}{dq}Y_{\nu'}(\alpha,q)\,d\alpha. \tag{17}$$

This matrix is the analogue of the one introduced by Smith [34] for the treatment of nonadiabatic (diabatic) couplings in atomic collisions. It is familiar also in

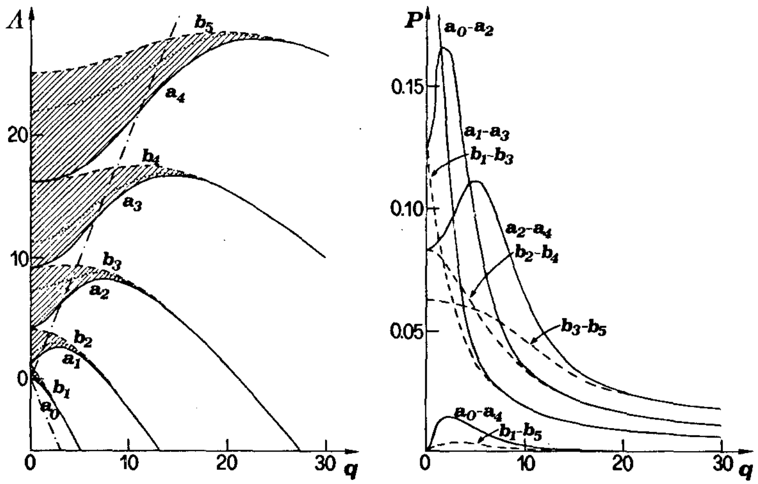


Fig. 2. Some eigenvalues of the Mathieu equation, as a function of the parameter q, are reported on the left together with the ridge line $2q$ and the valley bottom line $-2q$ (*dash-dotted*). Eigenvalues corresponding to $\beta = 2/3$ and $4/3$ are shown by *dotted lines*. Allowed regions for eigenvalues are *hatched*. The right-hand side shows elements of the P matrix as a function of q

molecular structure problems, where it indicates local breakdowns of the Born-Oppenheimer approximation. Within the hyperspherical formalism [17], it has been studied in the three-body Coulomb problem [16, 35] and in chemical reaction theory [30-33]. Also, from Eq. (6)

$$P_{\nu\nu'}(q) = (\Lambda_\nu - \Lambda_{\nu'})^{-1} \int_0^{2\pi} 2Y_\nu(\alpha, q) \cos 2\alpha Y_{\nu'}(\alpha, q)\, d\alpha. \tag{18}$$

It is then possible to show, from properties of Mathieu functions Y_ν [26], that, for $q = 0$,

$$P_{\nu\nu'}(0) = (\nu^2 - \nu'^2)^{-1} \delta_{|\nu-\nu'|,1}.$$

The actual computation of the P matrix was performed using the matrices T of the coefficients $t_{2r,\nu}$ of the diabatic expansion in Eq. (17). From Eq. (17), which in matrix notation becomes (see also Eq. (8))

$$P(q) = \tilde{T}(q) \frac{d}{dq} T(q), \tag{19}$$

we obtain P from computed T by diagonalization at two close q values:

$$P(q) = \varepsilon^{-1}[\tilde{T}(q) T(q+\varepsilon) - 1], \tag{20}$$

where ε is a small number. From Eq. (18) we have, after some manipulation, the alternative formula

$$P_{\nu\nu'}(q) = [\Lambda_\nu(q) - \Lambda_{\nu'}(q)]^{-1} \left[\tilde{T}(q) \frac{dV}{dq} T(q)\right]_{\nu\nu'}, \tag{21}$$

where $dV_{\nu\nu'}/dq$ is simply $\delta_{|\nu-\nu'|,1}$. This formula has the advantage of requiring a single diagonalization at each q, and therefore becomes more convenient than

Eq. (20) as the size of the secular problem increases. The left-hand side of Fig. 2 shows some computed $\boldsymbol{P}$-matrix elements: maxima at the ridge, to be expected from the corresponding minima in the eigenvalue differences (Eq. (21)) and other general properties, are clearly displayed in Fig. 2.

We conclude by commenting briefly on the role of sequences of avoided crossings along the ridge, and on the related question of whether analytic continuation would reveal true crossings for complex values of q. Recent results [36] on the analytic continuation of the eigenvalues of the Mathieu equation are motivated by the fact that their crossings in the complex q-plane are related to the convergence radii of perturbation expansions. Therefore, it is not surprising to find that there is a correspondence between real parts of complex crossings, as listed in [36], and positions of the maxima in elements of the matrix $\boldsymbol{P}$ as defined in this work (see also [12]).

Actually, the semiclassical formulas discussed in [12] (see the previous section), although valid only asymptotically, are in a form which appears to be suitable for extensions in the complex q-plane. It would be interesting to investigate this aspect further, since analytic continuation plays a role in theories of nonadiabatic transitions [37]. This role which has not been firmly assessed until now because in actual problems the analytic structure of numerically generated eigenvalues is poorly understood [38].

3.4. Quantum modes of anharmonically coupled oscillators

As anticipated, the preceding analysis of the pendulum quantum modes can be immediately used to provide the analytical adiabatic representation of the two dimensional (Hénon-Heiles) model for coupled oscillators, conveniently written in polar coordinates as in Eq. (2). By relating the polar variable ρ and the parameter q,

$$q=\frac{4}{27}\lambda\rho^5, \tag{22a}$$

and the angular variable θ with the angle α of Mathieu equation,

$$2\alpha=3\theta+\pi, \tag{22b}$$

Eq. (13) becomes Eq. (15). Therefore, the adiabatic potential energy curves $\varepsilon_\nu(\rho)$ are obtained from Mathieu eigenvalues $\Lambda_\nu(q)$ according to the formula

$$\varepsilon_\nu(\rho)=\frac{9}{8\rho^2}\Lambda_\nu(q)+\tfrac{1}{2}\rho^2. \tag{23}$$

The elements of the nonadiabatic coupling matrices are likewise related:

$$P_{\nu\nu'}(\rho)=\frac{dq}{d\rho}P_{\nu\nu'}(q)=\frac{20}{27}\lambda\rho^4P_{\nu\nu'}(q). \tag{24}$$

Figures 3-5 are obtained from these formulas using computed eigenvalues and eigenvectors of Mathieu equation.

A useful aspect of this approach is to provide a classification scheme for levels. When $\lambda=0$ (the simple isotropic oscillator) a good quantum number exists, and it is designated by $\pm l$ in [4]. For finite λ the potential belongs to the C_{3v} symmetry group and the wavefunctions are classified according to its irreducible representations $\mathscr{A}_1, \mathscr{A}_2$ and $\mathscr{E}$. Mathieu functions ce_{2n} and se_{2n} behave as $\mathscr{A}_1$ and $\mathscr{A}_2$ respectively under the C_{3v} symmetry operations. Their eigenvalues are labelled as A_{2n} and B_{2n+2}, where $n = 0, 1, 2, \ldots$ (Fig. 2), they have a periodicity of π, and correspond to $\beta = 0$. The $\mathscr{E}$ representation is induced by Mathieu functions of fractional order $ce_{2n+\beta}$ and $se_{2n+\beta}$, and the corresponding doubly degenerate eigenvalues will be designated as $\Lambda_{2n+\beta}$. For this symmetry β can assume only the values 2/3 and 4/3, and in order that the proper boundary conditions are satisfied, the functions will have periodicities 3π and $3\pi/2$. Therefore, the levels supported by each adiabatic curve will be conveniently labelled by both the proper index of corresponding Mathieu functions $2n+\beta$, and by a progressive number $v = 0, 1, 2, \ldots$. The Mathieu index is related to l by $|l| = 3n + \beta/2$ and in the isotropic oscillator limit ($\lambda = 0$) the energy levels are given by the formula $2v + 1 + |l|$.

As illustrated in Fig. 3, failures of the adiabatic picture, which can be measured from the elements of the matrix for nonadiabatic coupling $\boldsymbol{P}$, occur at the ridge. The correlation between regular modes of classical investigations and the quantum mechanical states which are localized above the ridge has already been pointed out [5]. In our picture, quantum mechanical delocalization of the wavefunction is a process which is favored by a coupling between the adiabatic eigenvalues in the proximity of the ridge, where a sequence of level interactions shows up, and corresponds to maxima in the $\boldsymbol{P}$ matrix. These features should be discussed within the framework of the theory of nonadiabatic interactions, and a striking similarity is apparent between these aspects and the spectroscopic level perturbation for diatomic molecules [40a]. Actually, our current experience suggests that the semiclassical techniques introduced in such a context are also extremely fruitful here.

An adiabatic approximation (i.e. a single term in expansion (1)) is not only qualitatively justifiable for characterizing the nature of quantum states far from ridge, but has also been found to be excellent for quantitative semiclassical quantization [40b]. For the lowest two states of $\mathscr{A}_2$ symmetry in Fig. 3, we obtain values of 3.9837 and 5.8840 by one-dimensional WKB (which is essentially a Bohr-Sommerfeld rule in this case), which may be compared with the exact values of 3.9858 and 5.8815 respectively; this is significantly better than any previous semiclassical recipe [41]. However the procedure will fail for higher states when nonadiabatic effects associated with the ridge come into play and invalidate the assumption of separability.

Figure 4, which reports similar results for the $\mathscr{E}$ symmetry, focuses attention on a particularly interesting type of avoided crossings, due to the interaction between almost degenerate levels, that is supported by the adiabatic curves. This phenomenon leads to much more pronounced delocalization of the wavefunctions because of the strong mutual perturbation of the levels, and is strongly dependent on the parameter λ, which measures the strength of the coupling between the oscillators. Therefore, it is relevant to extended discussions [41, 42] of the role

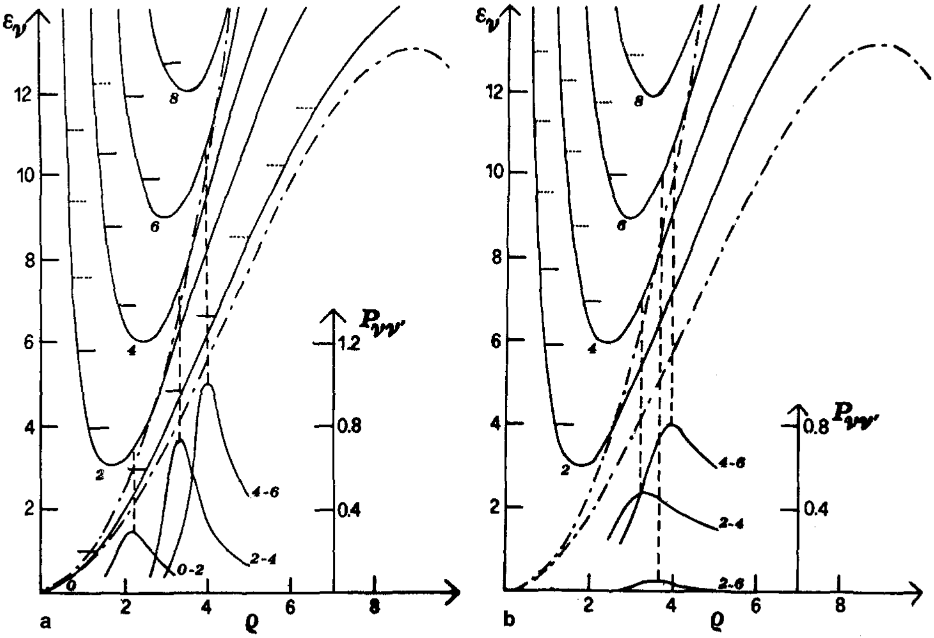


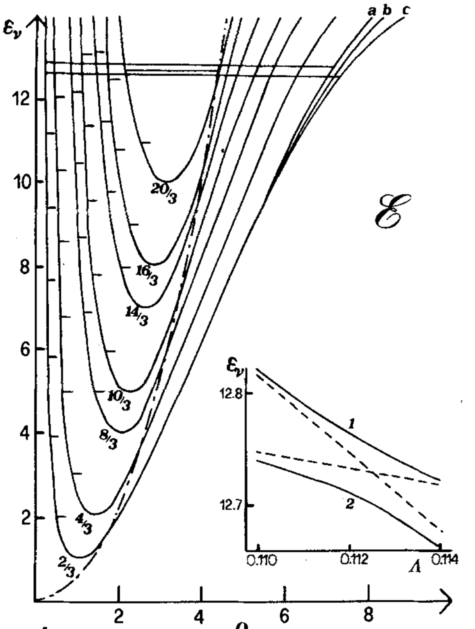
Fig. 3. **a** $\mathscr{A}_1$; **b** $\mathscr{A}_2$. For the Hénon-Heiles potential with $\lambda = 80^{-1/2}$ (Eq. 2): *Upper broken curve*, ridge profile ($\theta = \pi/3, \pi, 5\pi/3$); *lower broken curve*, valley bottom profile ($\theta = 0, 2\pi/3, 4\pi/3$)), adiabatic potential energy curves $\varepsilon_v(\rho)$ (Eq. 23) and corresponding nonadiabatic coupling matrix elements $P_{vv'}(\rho)$ (Eq. 24) as a function of radial coordinate ρ for $\mathscr{A}_1$ and $\mathscr{A}_2$ symmetry. Positions of levels indicated by *continuous segments* for those identified as quasiperiodic [39] and by *dotted segments* for those not identified as quasiperiodic

of avoided crossings as a function of the parameter λ. In the present approach, such avoided crossings, earlier noted by Percival [43], to be a road to quantum chaos, are seen to arise when, because of the increasing importance of anharmonicity for levels with high v quantum numbers, high v levels of lower curves enter into accidental resonance with low v levels of upper curves. This phenomenon, which can be related to similar effects in molecular spectroscopy [42], leads to strong level repulsion [42]. For the model considered here, this phenomenon happens once in the neighborhood of $\lambda = 80^{-1/2} = 0.118$ (Fig. 4).

4. Semiclassical analysis of resonances

4.1. *The quantum resonance theory of unimolecular reactions*

The previous analysis is of interest not only for general mode transition problems, but also for providing a useful model for unimolecular reaction theory. Consider again the potential given by Eqs. (1) and (2), and illustrated in Fig. 1. If its behavior is examined at large ρ values, it is seen that it has three symmetric saddles of height $(6\lambda^2)^{-1}$ at $\rho = \lambda^{-1}$, and eventually goes to minus infinity. Therefore all the states which it supports are actually metastable, and they will eventually decay by quantum mechanical tunneling: In other words, they are typical quantum mechanical resonances, to which we may associate a width Γ



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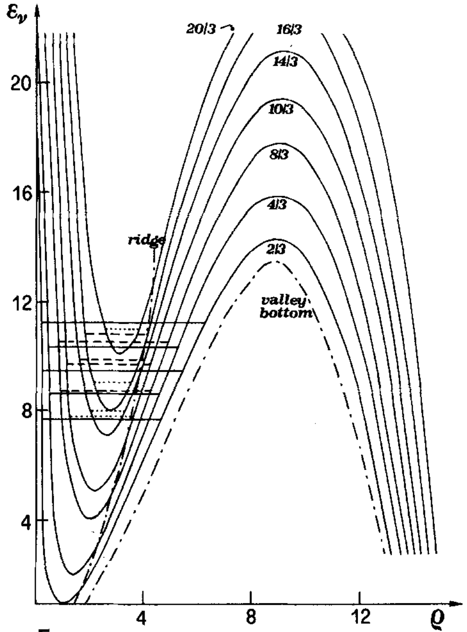

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Fig. 4. Adiabatic curves $\mathscr{E}_\nu(\rho)$, Eq. (23), for the ε symmetry of Hénon-Heiles potential (Eq. 2) for λ close to $80^{-1/2}=0.1118$. Slight changes in λ mainly affect the large ρ region: for example, the curves labelled as *a*, *b*, and *c* show how the 2/3 state changes for $\lambda=0.110$, 0.112, 0.114. The corresponding $\nu=7$ level varies as in inset, and thus would cross the $\nu=2$ level of the 20/3 state, which is practically unaffected by a change inλ [42] (*dashed curves*): Actually, the crossing is avoided and the levels behave as the continuous curves 1 and 2 [42]
The correspondence with classical chaos and *N* (nonperiodic) quantum modes is then with strongly delocalized wavefunctions described by a superposition of modes nonadiabatically coupled in the ridge region

Fig. 5. Behavior, at larger ρ, of some of the curves in Fig. 4. *Dotted continuous* and *dashed lines* indicate states designated as Q_I, Q_{II} and *N*, respectively in [5] (see also [39])

and a lifetime $\tau=\hbar\Gamma$. This model has already been considered [10, 11] for unimolecular reaction theory, where the resonance lifetime is most naturally related to the inverse of the unimolar rate constants $k=\tau^{-1}$ (see also [13]).

In a search for mode specificity in resonances, we extend the previous analysis to larger ρ values, obtaining for the E symmetry, for example, the curves depicted in Fig. 5. Also shown in Fig. 5 are some levels considered in [11], and their classification in terms of Q_I, Q_{II} and N states [39] is also indicated. Bai et al. [11] find strong mode specificity for this system: The Q_{II} states show the largest unimolecular rate constants, the Q_I states the smallest, and the N states show an intermediate behavior. (Here, as often [10, 11], nonspecificity means dependence on energy only; it is assumed to be an indication of full energy randomization in the molecules and therefore a good measure of the appropriateness of statistical arguments.)

Figure 5 shows that the results of [5] can be qualitatively understood by considering again the ridge effect; in particular, it is apparent that Q_{II} states, being characterized by higher vibrational numbers of lower curves, have their outer turning points well beyond the ridge and may therefore undergo extensive nonadiabatic transitions to the lowest curve, from which tunneling to dissociation is clearly easier. Conversely, Q_I states are confined inside the ridge and thus present the lowest decomposition rates. The N states, for which the outer turning point is close to the ridge, clearly have strong coupling between adiabatic states, and the associated lifetimes are intermediate between the extremes.

A quantitative semiclassical analysis of these effects for this model and similar ones, in particular for a recent model for the reaction $CH_2O \to CO \to H_2$ [10, 44], is reported elsewhere [13]. The two-dimensional model surface has C_{2v} symmetry. This analysis is based on a well known semiclassical formalism for resonance positions and widths [45]. It leads to quantitative agreement with the RRKM theory in the complete randomization hypothesis and it points out the role of ridge effects for such a randomization. The conditions for mode specificity are also analyzed; an important aspect of this approach is that mode specificity due to symmetries in the transition state [46] arises in a natural way through the group theoretical labelling of the Mathieu functions outlined in the previous section.

4.2. Resonance widths in the adiabatic limit

As illustrated in Figs. 1 and 4, adiabatic states as a function of ρ exhibit a well and a barrier, and nonadiabatic couplings between states are localized around the ridge profile. Semiclassically [14] the probability of tunneling through a barrier of height E_ν and complex barrier frequency $i\omega_\nu^*$ for the ν-th adiabatic state $\varepsilon(\nu = 0, 1, 2, \dots)$ is

$$p_\nu(E) = \exp[2\pi(E - E_\nu)/\hbar\mu_\nu^*, \tag{25}$$

where E is the energy. From asymptotic properties of Mathieu eingenvalues [26, 28] in this case we have $\hbar\omega_\nu^* = 1$, and the adiabatic thresholds (barrier heights) are $E_\nu = (6\lambda^2)^{-1} + (\nu + 1/2)\sqrt{3}$. Symmetry enters through ν: symmetry states $\mathscr{A}_1$, or $\mathscr{A}_2$ correspond to even and add ν respectively, while any ν is allowed for the degenerate states $\mathscr{E}$. In particular, the lowest adiabatic barriers for $\mathscr{A}_1$ and $\mathscr{E}$ symmetries both correspond to $\nu = 0$.

In the adiabatic limit, resonance widths may be obtained by a one channel formula [13]:

$$\Gamma_\nu(E) = \frac{\hbar\omega_\nu[(1+p_\nu)^{-1/2} - 1]}{2\pi[(1+p_\nu)^{-1/2} + 1]}, \tag{26}$$

where for the frequency at the bottom of the adiabatic wells we can use the estimate $\hbar\omega_\nu = 2$, again exploiting properties of Mathieu eigenvalues [26, 28].

Alternatively the same ingredients can be inserted in a RRKM type of formula, corrected for tunneling according to Miller [9, 10, 13]:

$$\Gamma_\nu(E) = (2\pi(E/m)(1 + p_\nu^{-1})]^{-1} \tag{27}$$

where E/m is our result (see Figs. 2-5) for the density of states in the neighborhood of total energy E. The symmetry factor m is four for classes $\mathscr{A}_1$ and $\mathscr{A}_2$, and two for $\mathscr{E}$ (in [10] m was taken to be three for all classes, so this specific symmetry dependence was lost).

Results from both formulas are shown in Fig. 6 for $\lambda^2 = 0.02$, and comparison with the exact values [10, 11] available for this system indicates that both reproduce magnitudes and trends. Similar agreement was found for the values 0.03 and 0.04 (also considered in [10]); the results are not reported for brevity.

The present analysis stresses the role of tunneling under adiabatic saddles whose characteristics depend on symmetry in a way which our approach exploits most simply. In systems such as these, exhibiting a relatively small density of states, the difference between preexponential factors in the two formulas does not lead to significant differences in calculated widths. Also, fluctuations around the predicted average behavior are within numerical error in these cases. Indeed, wider fluctuations were found [11] for $\lambda^2 = 0.0125$, a case where the density of states is higher (see Figs. 3-5 and previous section). Such fluctuations correlate with the regularity of states in a way that our adiabatic analysis explains qualitatively (see Sect. 4.1, [47]); however, the explicit introduction of the nonadiabaticity associated with the ridge effect is required to account quantitatively for these fluctuations. Their origin is rooted in the mechanism for the redistribution of energy among modes, which is not described at the adiabatic limit considered here; more elaborate models are required, such as Miller's semiclassical perturbation-infinite order sudden approximation [48], or, more simply, our sudden limit formula [13].

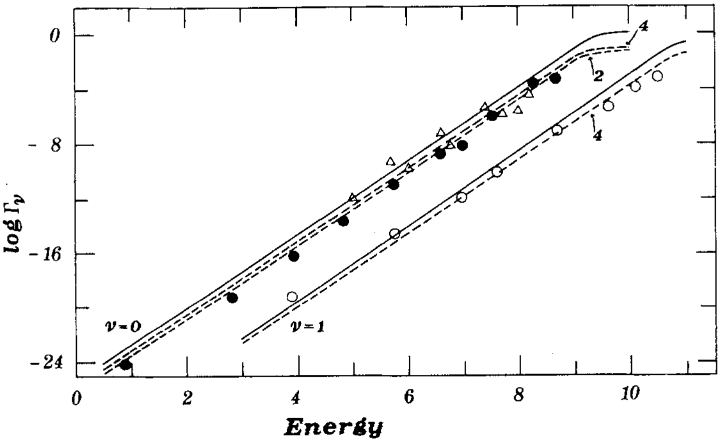

Fig. 6. Hénon-Heiles, $\lambda^2 = 0.02$. Resonance widths $\Gamma_\nu(E)$ ($\nu = 0$ for $\mathscr{A}_1$ and $\mathscr{E}$, $\nu = 1$ for $\mathscr{A}_2$) in the adiabatic limit (Eq. (26), *continuous curves*) and RRKM (Eq. (27), *dashed curves*, labelled by $m = 4$ for $\mathscr{A}_1$ and $\mathscr{A}_2$, and $m = 2$ for $\mathscr{E}$). *Dots* and *triangles* are the exact results from [10] for $\mathscr{A}_1$ and $\mathscr{A}_2$ symmetries and from [11] for $\mathscr{E}$ symmetry

5. Concluding remarks

The adiabatic representation in radial polar coordinates can be formulated for the Hénon-Heiles model potential by using analytical properties of Mathieu functions. Qualitative properties of modes of anharmonically coupled oscillators are made especially transparent by this analysis. The connection between the quasiperiodic and chaotic trajectories of classical mechanics and the regular and irregular quantum modes is interpreted in terms of the characteristics of adiabatic curves (Figs. 3-5). Nonadiabatic coupling, which is strongest at ridges in the potential, is characterized as a source of irregularity.

The short wave asymptotic nature of this procedure can be proven following, for example, [49]. Therefore under semiclassical conditions it is particularly convenient to exploit the quasiseparability of a variable. For problems of higher dimensionality, a strategy involving a hierarchy of successive approximate separations can be devised (see, e.g., [50]).

Appendix: The Hénon–Heiles potential and the elliptic umbilic catastrophe

It is interesting to note the connection between the Hénon-Heiles potential considered in this paper (Eq. (1), Fig. 1) and the elliptic umbilic catastrophe function $D_{-4}(x, y; a, b, c)$ [2, 51], where x, y are the Cartesian coordinates and a, b, c are the control parameters:

$$V(x, y; \lambda) = \lambda D_{-4}(x, y; (2\lambda)^{-1}, 0, 0), \tag{A1}$$

i.e. $a = (2\lambda)^{-1}$, $b = 0$, $c = 0$.

Catastrophe theory classifies functions exhibiting topologically canonical features. Its use in quantum mechanics has many facets; typically it provides an elegant classification [52] of canonical integrals which describe interference and diffraction effects in wave mechanics, in analogy to the corresponding effects of wave optics [53].

Here we are pointing out a different application, namely the study of the time-independent mechanics for potentials which are isomorphic to catastrophe functions. Because of the canonical nature of the latter, it can be argued that such a study, when carried out systematically, will provide a full qualitative description of quantum mechanical behavior for a wide variety of problems. Moreover, an important technique for effective solution of the time independent Schrödinger equation in the semiclassical (short wave) limit is to provide solutions to *canonical* models which exhibit the same structure (e.g. distribution of turning points) as the problem at hand and then to provide a mapping procedure (e.g. matching of phase integrals). This asymptotic technique of reference equations [54] is well founded in one dimensional problems, where it is a generalization of the WKB method to obtain scattering phase shifts, and of Bohr-Sommerfeld quantization to obtain bound states. Canonical reference equations are Airy and Weber differential equations. They allow the full analytical solution of the related Stokes phenomenon for the uniform asymptotic representation of one and two turning point problems respectively. Similarly a study of the fold function (the simplest catastrophe) provides the canonical form for three turning point problems and therefore the description of resonance scattering. Since the solutions of the corresponding Schrödinger equation, which involve a cubic coefficient [55], are only known in regions away from the fold catastrophe (transition from one to three turning points) a reliable analysis is available only in limiting cases.

An analysis of quantum mechanics for the cusp-like potential function (four turning points) has been presented recently [56]; it can be shown [57] that wave mechanics *avoids the catastrophe*, namely positions of bound states vary smoothly across the transition from a single well (two turning points) to two wells (four turning points). This is a further example of how quantum mechanics behaves well when classical mechanics has trajectories which are sharp separatrices between modes (see Sect. 2.2 for the pendulum motion).

For two-dimensional extensions, the simplest are the umbilic catastrophe functions, still to be studied from this viewpoint. However, the function dual to D_{-4},

$$D_{+4}(x, y;\, a, b, c) = x^2y + \tfrac{1}{3}y^3 + a(x^2 + y^2) + bx + cy \tag{A2}$$

(for $c = b = 0$ sometimes known as the Anti-Hénon-Heiles potential [58]), under the change of variables

$$x = \frac{1}{\sqrt{2}}(X + Y) \quad \text{and} \quad y = \frac{1}{\sqrt{2}}(X - Y)$$

transforms into the sum of two cubics in X and Y. Therefore the corresponding potential allows exact separation and its study reduces to that of two separate cusp functions.

In this vein, the present study (and all the related ones on Hénon-Heiles coupled oscillators) are steps towards the characterization of the elliptic umbilic topology for potential energy surfaces (such as for the interaction of three atoms, as pointed out recently [8]). Specifically, we have provided in this paper an analysis for the quantum mechanical modes away from the catastrophe point $a = 0$ (or $\lambda \to \infty$), and in particular we have considered positive values for the control parameter (a or λ) in a range where the topological structure (three saddles and one minimum) is preserved.

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