

Periodic Orbit Assignment for Spectra of Highly Excited Molecular Systems

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Periodic orbit assignment for spectra of highly excited molecular systems

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Recent experiments in high-energy molecular spectroscopy have shown that coarse grained molecular spectra are often very simple, characterized by a few frequencies or correlation times. Experiments in molecular scattering such as the hydrogen exchange reactions have demonstrated the existence of short-lived resonances. I show that these seemingly differing experiments may be interpreted and assigned in terms of the normal modes of periodic orbits, which are determined by a linear stability analysis. Specific examples include three-dimensional resonances of the hydrogen exchange reaction as well as three-dimensional high-energy bound states of the H_3^+ molecular ion. A new semiclassical quantization method based on unstable periodic orbits is presented and used to explain the observed scarring of high-energy quantum states.

1. Introduction

The standard approach to analysis of molecular spectra is an expansion about the normal modes of the molecule. These are determined by finding the minimum of the Born–Oppenheimer potential energy surface, expanding up to quadratic terms about the minimum and diagonalizing the resulting quadratic hamiltonian (Wilson *et al.* 1955). Nonlinear corrections are then found by extending the normal mode approach, using for example a Darling–Dennison expansion (Darling & Dennison 1940). This methodology has been extremely useful to spectroscopists and serves as the basis for analysis of experimental spectra.

The high overtone spectra of some simple molecules such as H_2O or C_2H_2 have revealed that at times it is more convenient to analyse spectra in terms of local bond stretching modes such as an OH stretch or a CH stretch (Lawton & Child 1979, 1980, 1981). Much work has been devoted in recent years towards understanding these two different approximations. Analysis of the classical dynamics of these types of molecules has shown that at very low energies one will usually find as many periodic orbits as there are normal modes. For example, in CO_2 one will find a symmetric and antisymmetric stretch periodic orbit. However, as energy is increased, the symmetric stretch orbit undergoes a bifurcation giving two new orbits, which correspond to the local mode motion in the sense that their configuration space path is roughly along the local bond stretch (Lawton & Child 1979, 1980, 1981). Although two different classification schemes do lead to complications, recent work by Kellman (1985) has shown that the nonlinear terms in the normal mode expansion of the hamiltonian will give at higher energies local mode type motion, thus ‘rescuing’ the normal mode approach to molecular spectroscopy.

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Six years ago, Carrington & Kennedy (1984) reported their study of the photodissociation spectrum of the H_3^+ molecular ion. They found approximately 27 000 lines corresponding to transitions between metastable states (with respect to dissociation into $\text{H}_2 + \text{H}^+$) confined to a spectral region of less than 300 cm^{-1} . Assignment of these lines was impossible. Amazingly though, upon suitable coarse graining of the spectrum, they found a very simple structure, four somewhat broadened peaks with a constant spacing of 53 cm^{-1} . This spacing has nothing in common with the normal mode frequencies of ground state H_3^+ .

Since then a number of other high energy molecular spectra have been measured in some detail, usually using the stimulated emission pumping (SEP) technique pioneered by Field, Kinsey and co-workers in their study of the high energy spectrum of acetylene (Abramson *et al.* 1985). Other examples, are the SEP study of the Na_3 molecule by Whetten, Wöste and co-workers (Broyer *et al.* 1989) and the absorption spectrum of O_3 in the Hartley band (Freeman *et al.* 1984). In all these cases, the spectra include many lines that seem to be unassignable; however, coarse graining or limited Fourier transforms of the spectra reveal characteristic frequencies and correlation times that are not necessarily related to the normal modes of the molecule.

The 'simplest' example for this type of behaviour is the high energy absorption spectrum of the hydrogen atom in a strong magnetic field (the quadratic Zeeman effect (QZE)) measured by Welge and co-workers (Holle *et al.* 1988 and reference therein) and analysed theoretically in great detail by Wintgen (1988) and co-workers. A limited Fourier transform of the spectrum revealed correlation times which could be identified with periods of a class of periodic orbits. Quantum mechanical studies showed that wavefunctions tended to scar around these unstable orbits, in a manner reminiscent of the scarring found by Heller (1984) in his study of quantum billiards.

Much theoretical and experimental work has been devoted in recent years to transition state spectroscopy. Here one is attempting to probe the dynamics of a short-lived intermediate in a reactive process. A recent experimental result has been obtained by Nieh & Valentini (1988), who detected structure in the reactive cross-section that may be attributed to the resonances found in theoretical computations of the reaction probability. These resonances were first noted in collinear $\text{H} + \text{H}_2$ scattering computations (Wu *et al.* 1973; Schatz *et al.* 1973) but have subsequently been shown to exist also in the full three-dimensional scattering dynamics (Walker *et al.* 1978; Webster & Light 1986). In common with the spectra of high-energy molecules, the spacings between various resonance energies are not related directly to either the asymptotic properties of the reactant or product molecules nor to the normal mode frequencies of the saddle point of the potential energy surface.

Pollak & Child (1981) provided an assignment of the collinear resonance energies in terms of what they called a resonant periodic orbit (RPO) whose motion corresponds to a strongly perturbed antisymmetric stretch motion. The major qualitative difference between the RPO and normal mode or local mode orbits found in bound molecules is that the RPO is unstable, classical trajectories initiated in its vicinity move away from the orbit, ultimately dissociating. This analysis revealed a 'scarring' of the quantum resonance wavefunction about an unstable periodic orbit, prior to the discovery of scars in the billiard problem (Heller 1984).

More recent three-dimensional computations showed the full structure of the resonance. The peaks in the time delay found by Kuppermann and co-workers (Cuccaro *et al.* 1989) give a well defined theoretical determination of the three-

dimensional resonance energies. These peaks can be assigned in terms of the properties of the RPOs (Pollak & Wyatt 1982, 1984; Pollak 1986). Specifically, linearizing the classical equations of motion around the RPO enables the determination of the stability frequencies of the orbit. All resonance energy spacings found in the zero total angular momentum computations were assigned accurately in terms of these frequencies. The dependence of the resonance energies on the total angular momentum was also predicted from the average moment of inertia of the RPOs and was subsequently found to be in good agreement with exact quantal three-dimensional computations (Zhao *et al.* 1989). The resonance spectrum of the hydrogen exchange reaction is the first example of periodic orbit assignment of a high energy species, here the energy is so high that the species is only short lived, of the order of one or two vibrational periods of the RPO.

The purpose of this paper is to suggest that periodic orbit assignment of coarse grained spectra is the natural extension of the normal mode assignment of low-energy spectra. The normal mode method is based on an harmonic expansion around a stationary point of the potential energy surface. For small molecules, this is the unique minimum of the surface. As energy is increased, one moves far away from this minimum. However, even at high energies the classical dynamics do have invariant objects, these are the periodic orbits. A harmonic expansion about the periodic orbits provides what may be called the local normal modes of the periodic orbit. In this paper we will demonstrate, for a number of systems, that these local normal modes can provide the basis for analysis and assignment of high-energy coarse-grained spectra. The numerical results described in this paper have been reported previously elsewhere. The new elements presented in this paper are: (a) the unifying principle; seemingly diverse systems are found to have a common element, assignment in terms of local normal modes of periodic orbits, and (b) a new periodic orbit quantization method is presented. This method provides insight into quantum localization around unstable periodic orbits.

In §2 we review recent results found for resonances in reactive scattering. These include the hydrogen exchange reaction for which the surface is characterized by a saddle point, and a model two-degree-of-freedom system which involves reaction on a surface with a relatively deep potential energy well mediating between reactants and products. In §3, we move to a bound state system, assigning the quantum states of the two degree of freedom hamiltonian of $C_{2v}H_3^+$ as well as the non-rotating three-dimensional high-energy states of H_3^+ . In §4 we review briefly recent results on a model two degree of freedom problem involving a quartic potential energy surface, and propose a new method for periodic orbit semiclassical quantization which is applicable to families of unstable periodic orbits.

2. Resonances in reactive scattering

(a) Linear stability analysis of periodic orbits

The main theme of this paper is that a linear stability analysis of periodic orbits provides the normal mode frequencies which appear in high energy molecular spectra. We review briefly the main elements of stability analysis of periodic orbits (Miller 1975). Consider a system with N degrees of freedom, described by coordinates q_i , conjugate momenta p_i ($i = 1, \dots, N$) and hamiltonian $H(\mathbf{q}, \mathbf{p})$. A periodic orbit is a classical trajectory that originates at time $t = 0$ at the phase space point $(\mathbf{q}_0, \mathbf{p}_0)$ and

returns to it at time T . The frequency of the orbit is denoted $\omega = 2\pi/T$. Linearizing the equations of motion about the orbit leads to the $2N \times 2N$ matrix differential equation

$$d/dt R(t) + F(t) R(t) = 0, \quad R(0) = I, \quad (1)$$

where the $2N \times 2N$ force constant matrix $F(t)$ is determined by the second derivatives of the hamiltonian, taken along the periodic orbit,

$$F = \begin{bmatrix} -\partial^2 H / \partial \mathbf{p} \partial \mathbf{q} & -\partial^2 H / \partial \mathbf{p}^2 \\ \partial^2 H / \partial \mathbf{q}^2 & \partial^2 H / \partial \mathbf{q} \partial \mathbf{p} \end{bmatrix} \quad (2)$$

and I is the $2N \times 2N$ identity matrix. Integrating (1) for one period gives the matrix $R(T)$ which has $2N$ eigenvalues that come in pairs denoted $e^{\pm u_i}$ ($i = 1, \dots, N$). The exponents u_i are known as the characteristic exponents. The eigenvectors associated with the eigenvalues are the periodic orbit analogues of the normal modes. The important properties associated with the characteristic exponents are:

- (a) if $\text{Re } u_i = 0$ for all $i = 1, \dots, N$ then the periodic orbit is stable;
- (b) if for any i , $\text{Re } u_i \neq 0$ the orbit is unstable;
- (c) the characteristic exponents are invariant under a canonical transformation of coordinates and momenta.

Typically, there are no severe numerical complications involved in integrating the linearized equations. As long as the orbit and its period are known with sufficient accuracy any standard integration package, which is in any case used to find the periodic orbit, suffices. The only complication has to do with the absolute phase of the exponent. If the j th exponent is purely imaginary then any numerical method based only on the specific solution of the linearized equations can determine the phase up to mod (2π) . For the normal mode analysis it is necessary to determine the absolute phase. This may lead to some complications, whose solution is described in detail in Stefanski & Pollak (1987, 1989) and Tennyson *et al.* (1990). If the absolute phase ϕ_j is known, i.e. $u_j = i\phi_j$ then one may define the stability frequency of the j th mode as $\omega_s^j = \phi_j/T$.

A semiclassical approximation for energies of quantum states localized around the orbit is easily obtained in terms of the stability frequencies (Stefanski & Pollak 1987). One first quantizes the action J along the orbit, such that $J = (n + \frac{1}{2})\hbar$ at the energy E_n . The periodic orbit normal mode approximation for quantized energy levels is:

$$E_{nm} = E_n + \sum_{j=1}^{N-1} (m_j + \frac{1}{2}) \hbar \omega_s^j(E_n), \quad (3)$$

where note has been taken that the stability frequencies themselves will change with the energy of the periodic orbit. With each stability frequency there is associated an eigenvector that gives the direction in phase space of the local normal mode. Together they comprise the periodic orbit normal modes which can then be used to assign the coarse grained molecular spectra.

(b) Resonances of the $\text{H} + \text{H}_2$ reaction

The energy dependence of the quantum mechanical collinear (two degree of freedom) reaction probability of the $\text{H} + \text{H}_2$ reaction (on the PKII potential energy

Phil. Trans. R. Soc. Lond A (1990)

Table 1. RPO assignment of H+H₂ resonance energies^a

assignment	exact quantum ^b	RPO ^c	SCSA ^d
0, 0 ⁰ , 1	0.981	0.981	0.984
0, 2 ⁰ , 0	1.191	1.186	1.196
0, 0 ⁰ , 2	1.364	1.374	1.242
0, 2 ⁰ , 2	1.55 ± 0.03	1.545	1.464

^a All energies are in eV relative to the bottom of the asymptotic H₂ well, on the LSTH surface.

^b Zero total angular momentum exact quantum resonance energies as reported in Cuccaro *et al.* (1989).

^c RPO estimates of resonance energies (cf. Pollak 1986).

^d Estimates based on minimum energy path coordinates, taken from Garnett *et al.* (1984).

surface) showed peaks and dips at regular energy intervals of 0.43 eV (Wu *et al.* 1973; Schatz *et al.* 1973; Kuppermann *et al.* 1980). These undulations were interpreted as resonances, subsequent analysis of the quantum time delay matrix showed peaks in the time delay which coincided with the ‘bumps’ in the reaction probability. Analysis of the periodic orbits of the system revealed that the RPO had a frequency of $\omega = 0.215$ eV (Pollak & Child 1981). Since the reaction is symmetric, one expects that this frequency will lead to a spacing of resonance energies that corresponds to $2\hbar\omega$ in good agreement with the quantum results (similar agreement is also found for the LSTH potential energy surface). Since the motion of the RPO is a perturbed antisymmetric stretch one uses the standard spectroscopic notation and denotes this frequency as ν_3 .

The RPO is unstable with respect to perturbation in the collinear plane, however it is stable with respect to angular perturbation. The ‘bend’ stability frequency (on the LSTH surface) is found to be 0.090 eV and 0.081 eV for $\nu_3 = 1, 2$ respectively (Pollak 1986). The normal mode spectroscopic notation for this frequency is ν_2 . Recent full three-dimensional quantum computations at zero total angular momentum on the same surface revealed this predicted substructure of resonances energies (Cuccaro *et al.* 1989). In addition to the collinear spacing which had been associated with the antisymmetric stretch frequency, an additional smaller spacing had been observed, in good agreement with the ν_2 frequency predicted from the stability analysis of the RPO. In table 1 we list the observed three-dimensional quantum mechanical resonance energies, using the spectroscopic notation and compare with energies predicted from the normal mode analysis of the RPO. The RPO predictions are at present more accurate than any other adiabatic approximation method. For example, we also tabulate the SCSA results of Truhlar and co-workers (Garrett *et al.* 1984) which are based on an arbitrary coordinate system, guided by the minimum energy reaction path. For the lower resonances, they get reasonable results, but as the energy increases, the resonances move further away from the reaction path leading to substantial deviation from the exact quantum results. The RPO normal modes are energy dependent and account correctly for the higher energy resonances.

The rotational dependence of the resonance energy may be predicted in terms of the moment of inertia of the RPO (Pollak & Wyatt 1982, 1984). The rotational constant thus obtained for the (0, 0⁰, 1) resonance is 8 cm⁻¹ (Pollak & Wyatt 1982, 1984; Pollak 1986), in excellent agreement with recent full three-dimensional quantum computations (Zhao *et al.* 1989). (The rotational constant inferred from the results of Zhao *et al.* (1989) is 8.5 ± 1 cm⁻¹. It is interesting to note that Zhao *et al.*

Phil. Trans. R. Soc. Lond A (1990)

were not aware of the predictions for the constant presented in Pollak & Wyatt (1982, 1984) and Pollak (1986).) For resonance energies with higher values of the ν_3 quantum number, the RPO becomes more extended, with a larger moment of inertia so that the rotational constant decreases. For the $(0, 0^0, 2)$ resonance we predicted a rotational constant of 7 cm^{-1} , this prediction remains to be verified.

(c) *Resonances for collinear ABA molecules*

The structure of resonances for scattering of $A + BA$ on a potential energy surface with a deep well in the interaction region is much richer than in the case of a direct reaction such as $H + H_2$. Manz and co-workers (Bisseling *et al.* 1987) have published a series of papers in which they elucidated all collinear resonances found for a model $A + BA$ system, for which the potential surface exhibits a well depth of 0.76 eV . Many of the resonance wavefunctions were found to be localized around a hyperspherical radius, hence the name hyperspherical resonances (Bisseling *et al.* 1987).

We have recently studied the periodic orbit structure for this system (Stefanski & Pollak 1989) and found that the periodic orbit corresponding to the antisymmetric stretch normal mode at low energies, evolves into a hyperspherical like orbit as the energy is increased. Its motion in configuration space is actually quite similar to that of the RPO in the $H + H_2$ reaction, except that because of the well the energy in the mode is much larger. This orbit was found to be stable at all energies below the threshold of dissociation into $A + B + A$. Semiclassical quantization of the orbit, based on (3), gave excellent agreement with all hyperspherical quantum resonance energies, including cases in which the normal mode perpendicular to the orbit has an excitation. Since the range of energies spanned by this analysis is very large, one finds that the periodic orbit normal mode frequencies change by an order of magnitude, becoming smaller as the energy is increased. Here again, although the normal modes found at the bottom of the potential energy well are not relevant for analysing the high-energy dynamics, the periodic orbit normal modes are sufficient.

The usefulness of the periodic orbit normal modes might at first glance seem to be not too surprising. When an orbit is stable and the regular phase space surrounding it is large enough, one expects standard semiclassical EBK quantization (Lichtenberg & Lieberman 1983) to work. The linearization around the orbit provides a harmonic approximation to the EBK quantization. However, we also studied the phase space surrounding the orbit and found that at all energies above dissociation the regular part of phase space surrounding the orbit is substantially smaller than the $\pi\hbar$ needed for EBK quantization. Moreover, the shape of stable tori surrounding the orbit differs substantially from the elliptic form predicted by a harmonic expansion about the orbit. Thus although the classical analysis seemingly implies that the linearization about the periodic orbit will not work too well, we still find excellent agreement between the quantum resonance energies and the periodic orbit normal mode predictions.

3. High energy states of H_3^+

(a) *Reduced dimension C_{2v} states*

The coarse grained photodissociation spectrum of H_3^+ measured by Carrington & Kennedy (1984) has been recently assigned in terms of periodic orbit normal modes. Berblinger *et al.* (1988) in their (zero total angular momentum) classical study of the H_3^+ system, found a periodic orbit with C_{2v} symmetry which is stable in the full three-

Phil. Trans. R. Soc. Lond A (1990)

dimensional space. The motion of this orbit corresponds to a large amplitude bending motion of the molecule about the collinear plane. Since the configuration space path of the orbit in Jacobi coordinates resembles a horseshoe it was nicknamed the horseshoe orbit. Gomez Llorente & Pollak (1988, 1989) showed that this orbit remained stable even when the two outer hydrogen atoms were rotated such that the angular momentum vector was along the H^+ to the centre of mass of H_2 , coordinate (R). The rotational constant for this motion was 25–30 cm^{-1} (depending on the potential energy surface used) leading to a constant spacing of 50–60 cm^{-1} in the R branch associated with the infrared active antisymmetric stretch mode of the horseshoe orbit. The antisymmetric stretch (ν_3) frequency was found to be approximately 600 cm^{-1} . The coarse grained experimental spectrum was thus assigned as part of the R branch of the antisymmetric stretch mode of the horseshoe orbit with rotational quantum numbers in the range of 5.

This interpretation and assignment of the high-energy coarse grained spectrum relies heavily on the assumption that structure in high-energy spectra is a result of periodic orbit normal modes. Since the horseshoe orbit was found to be stable, it is plausible that it will give rise to structure in the spectrum, however, the quantum mechanism that leads to this structure has not yet been clarified. Taylor and coworkers (Taylor & Zakrzewski 1988; Gomez Llorente *et al.* 1989) have proposed that periodic orbits identify a region of classical phase space which is relatively decoupled from the rest of space. By using a Feshbach formalism, they construct a local basis set in this region which serves as a P subspace of resonance states which are then broadened by coupling to the background states. Applying these ideas to H_3^+ they showed (Gomez Llorente *et al.* 1989) that for motion restricted to the C_{2v} configuration one indeed finds stabilized quantum states localized around the horseshoe. Farantos and coworkers (Founargiotakis *et al.* 1989) have recently demonstrated quantum localization around periodic orbits, which is explained in terms of short-time classical localization.

To understand the connection between the periodic orbit normal mode picture and quantum mechanics, Tennyson *et al.* (1990) have studied in detail all the bound quantum states of H_3^+ in the reduced, two degree of freedom C_{2v} subspace. Two potential energy surfaces were used. The qualitative behaviour found on the accurate *ab initio* Meyer *et al.* (1986) (MBB) surface was very similar to that found on the more approximate diatomics in molecules (DIM) surface (Preston & Tully 1971). The advantage of the latter is that it is well defined for all energies while the MBB surface is well defined only up to 25000 cm^{-1} above the ground state. In the following we present results only for the DIM surface.

The quantum states of the C_{2v} hamiltonian have even and odd symmetry with respect to reflection about $R = 0$. A total of 148 bound states with odd symmetry were found. The typical structure of these wavefunctions is shown in figure 1 where the configuration space plots of 16 consecutive high-energy odd states are presented. Visual inspection shows that these states may be divided into three groups. States 113, 115, 116, 118–121, 123, 125, 126 and 128 have no clear nodal structure and so cannot be assigned in any obvious way. States 114, 122 and 127 are localized around the horseshoe orbit (shown as a solid line). State 114 has two excitations in the mode perpendicular to the orbit, state 122 has no excitations while state 127 has one excitation. By using the spectroscopic notation of ν_1 for the excitations perpendicular to the orbit, a nodal count shows that these states may be assigned as (2,14), (0,17) and (1,16) respectively. Their energies are 30980.7, 32124.4 and 32658.7 cm^{-1}

Phil. Trans. R. Soc. Lond A (1990)

respectively. A semiclassical quantization of the horseshoe orbit based on (3) gives the energies 31 324.5, 32 140.5 and 32 772.4 cm^{-1} respectively. Note the very good agreement between the semiclassical estimate and the exact quantum energy for the (0,17) state. This quality is typical of all horseshoe states with $\nu_1 = 0$. The average spacing between quantum levels in this energy region is 150 cm^{-1} so that the accuracy of the periodic orbit quantization is quite impressive. When the ν_1 mode is excited, the semiclassical estimate is not as good, the harmonic approximation consistently leads to an overestimate of the energy. Clearly, for these excitations, what is needed is an anharmonic expansion.

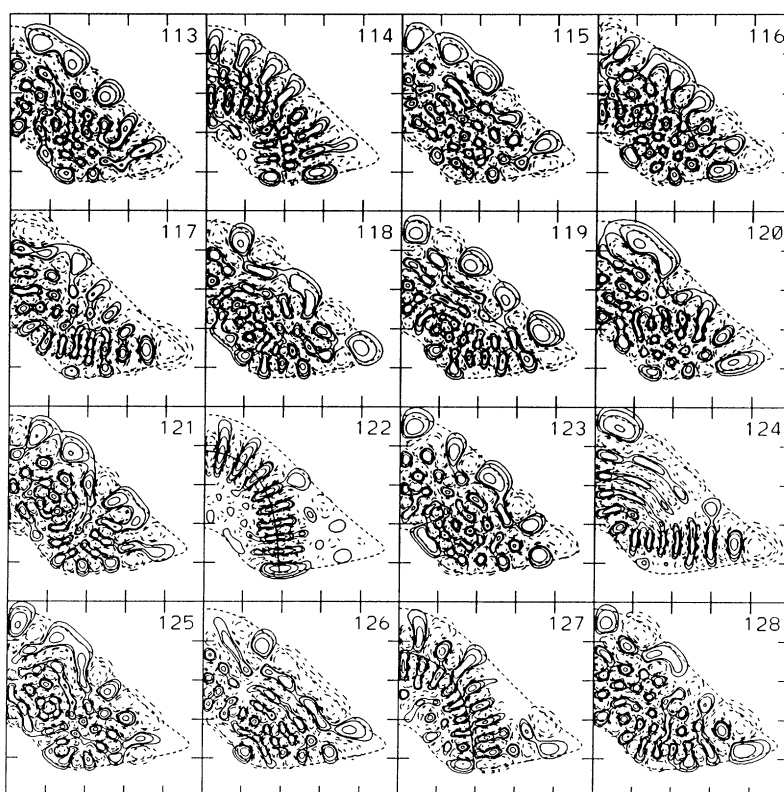


Figure 1. High-energy (odd) quantum states of C_{2v}, H_3^+ . The vertical and horizontal axes are the mass weighted coordinates \tilde{r}, \tilde{R} respectively, defined as $\tilde{r} = \alpha r, \tilde{R} = R/\alpha, \alpha = (\frac{3}{4})^{\frac{1}{2}}$. Here, r, R are the usual Jacobi coordinates, r is the distance between the two H atoms, R is the distance of H^+ to the centre of mass of the two H atoms. The C_{2v} configuration is such that r is perpendicular to R . The range is from 0–5 atomic units (a.u.), each tick mark denoting 1 a.u. Dashed and solid contours show negative and positive values of the wavefunction respectively and are at 0.64, 0.32, 0.16 and 0.08 of the maximum amplitude. The solid lines for states 114, 122 and 127 show the configuration space path of the quantized horseshoe orbit used to assign these states. Adapted from Brass *et al.* (1990).

The large number of unassignable states indicates that probably the majority of classical phase space is chaotic. We find, at this energy range that the regular region of phase space surrounding the horseshoe orbit is approximately $2\hbar$ which is less than the $\pi\hbar$ needed even for the ground ν_1 state. Thus the excellent agreement between the

Phil. Trans. R. Soc. Lond A (1990)

periodic orbit semiclassical quantization and the exact quantum energies remains a mystery, similar to the case of the resonances in ABA scattering presented in above.

States 117 and 124 shown in figure 1 are localized around what may be thought of as an inverted hyperspherical mode. The orbit corresponding to this motion is weakly unstable at these energies so that the localization is again poorly understood. Qualitatively, we expect the results presented here to be typical of high energy vibrations. Most states are unassignable, contributing to the Q space as a broad background. One does find though manifolds of states localized around some special periodic orbit families, these few families may be assigned in terms of the normal modes of their respective orbits.

(b) *Three-dimensional states of non-rotating H_3^+*

The classical study of the rotating horseshoe orbit (Berblinger 1988; Gomez Llorente & Pollak 1988, 1989) showed that it was stable even in three dimensions at energies close to the dissociation energy into $H^+ + H_2$. However, the orbit is not stable at all energies, it goes through alternating phases of stable and unstable behaviour, similar to the solutions of the Mathieu equation. Although three-dimensional surfaces of section were not computed, it was obvious that the stable area in phase space surrounding the orbit was much smaller (per degree of freedom) than in the C_{2v} case. A very small angular perturbation (typically of the order of 10^{-3} radians) away from the C_{2v} configuration sufficed to destabilize a trajectory. It was therefore of interest to see whether the quantum localization found in the reduced dimension C_{2v} system would persist also in three dimensions.

By using the three-dimensional programs of Tennyson & Henderson (1989), Brass *et al.* (1990) studied the three-dimensional quantum states of H_3^+ at $J = 0$. For states with energy up to 25000 cm^{-1} above the ground state, convergence of the order of 10 cm^{-1} was obtained, for higher lying states, we could not assure convergence in a variational sense. Even for these not fully converged states, the average spacing between adjacent energy levels at 3000 cm^{-1} below the dissociation threshold was approximately 25 cm^{-1} .

The projection of the three-dimensional wavefunctions on the \tilde{r}, \tilde{R} plane keeping the bend angle (γ) fixed was qualitatively very similar to the C_{2v} case. Most states were unassignable; however, a sequence of states localized around the horseshoe mode appeared very clearly. Changing γ by 30° away from 90° did not alter significantly the structure of these horseshoe states, indicating that they were in the ground state with respect to the antisymmetric stretch (denoted ν_3) motion. Although, as mentioned for high energies, the quantum computation was not fully converged, I believe that the energies and wavefunctions of the localized 'horseshoe states' are reliable in the sense of a stabilization computation. The basis set used, covers the horseshoe orbit region adequately. Indirect evidence for the adequate convergence was the fact that we could again obtain very good agreement between the periodic orbit based semiclassical prediction and the exact quantum energies.

There is, though, one major difference between the three-dimensional results and the C_{2v} case. In the three-dimensional case, the assignment provided by the periodic orbits was not unique. For example the semiclassical prediction for the energy of the (0,17,0) state was 35505 cm^{-1} . However, five quantum states, at the energies 35364, 35406, 35433, 35477 and 35542 cm^{-1} were found with the nodal structure that corresponds to this assignment. This result confirms the Feshbach resonance theory of Taylor and co-workers. We find that because of the high density of states, the

'resonance' state localized around the horseshoe has a 'width' and so has a non-negligible projection onto those quantum states whose energy roughly coincides with the resonance energy.

The main conclusions of the three-dimensional study are generally a reaffirmation of the results found in the C_{2v} case. A series of localized states could be identified and assigned through the nodal pattern. These states were localized around the horseshoe orbit even at energies for which the horseshoe orbit was unstable with respect to the ν_3 mode.

All these results corroborate the suggested interpretation for the experimental coarse grained spectrum. Close to the threshold for dissociation (at the energy of the $\nu_2 = 20$ orbit) the normal mode frequencies of the horseshoe orbit are 2632, 967 and 616 cm^{-1} respectively. These frequencies are still large in comparison with the rotational frequency of the rotating horseshoe orbit at $j = 5$, which is *ca.* 300 cm^{-1} . One may thus expect a good adiabatic separation between the rotational motion and the internal modes, leading to quantum localization around the horseshoe even in the presence of rotation.

It is to be expected that a ladder of localized states will lead to prominent features in the coarse grained spectrum. A recent reduced dimensionality study of the D_3^+ system (Sepulveda *et al.* 1990) demonstrates such a connection between the coarse grained spectrum and a ladder of localized states. In principle, one may find more than one type of localization as can be inferred from the C_{2v} wavefunctions presented in figure 1 (see especially states 117 and 124). However, in the three-dimensional study of the H_3^+ system we found that the only really recognizable ladder was associated with the horseshoe mode. Even if another ladder is found (my computations were not fully converged at the high energy end of the spectrum) it will not necessarily interfere with the coarse grained features associated with the horseshoe orbit localization. I thus conclude with the observation that the R branch of the spectrum associated with the ν_3 mode of the horseshoe orbit will lead to equally spaced peaks with a spacing of *ca.* $50\text{--}60 \text{ cm}^{-1}$. This provides an assignment of the experimental spectrum in terms of the horseshoe orbit normal modes.

4. A semiclassical theory of scars

(a) A quartic oscillator model

Perhaps the most puzzling aspect of all results presented thus far is the fact that quantum states localize around unstable periodic orbits. For the hydrogen exchange reaction this localization has been explained in terms of a vibrationally adiabatic well. Pollak & Römelt (1984) have demonstrated that the RPO lies at the bottom of a vibrationally adiabatic well so that although the orbit is unstable in the Liapunov sense it is stable in an adiabatic sense. A linear stability analysis reflects the infinite time behaviour of classical trajectories in the vicinity of the orbit. Quantum dynamics in the semiclassical limit are necessarily determined by finite time dynamics. If for finite time (usually of the order of a few periods of the orbit) one remains localized classically around the orbit then one may expect a quantum localization to occur. A plausible conjecture is therefore that the scars phenomenon is just a reflection of short time classical dynamics and will occur whenever the adiabatic stability of a periodic orbit is sufficient to localize classical trajectories in

the surrounding of the orbit for a time which is of the order of the period of the orbit itself.

To quantify this conjecture one needs to answer the following questions. (a) How does one obtain the best possible classical adiabatic breakup in the vicinity of the orbit? (b) How does one extract from this breakup an adiabatic hamiltonian which can then be quantized semiclassically? (c) How does one estimate the quality of the classical adiabatic approximation to determine whether or not quantum localization will occur?

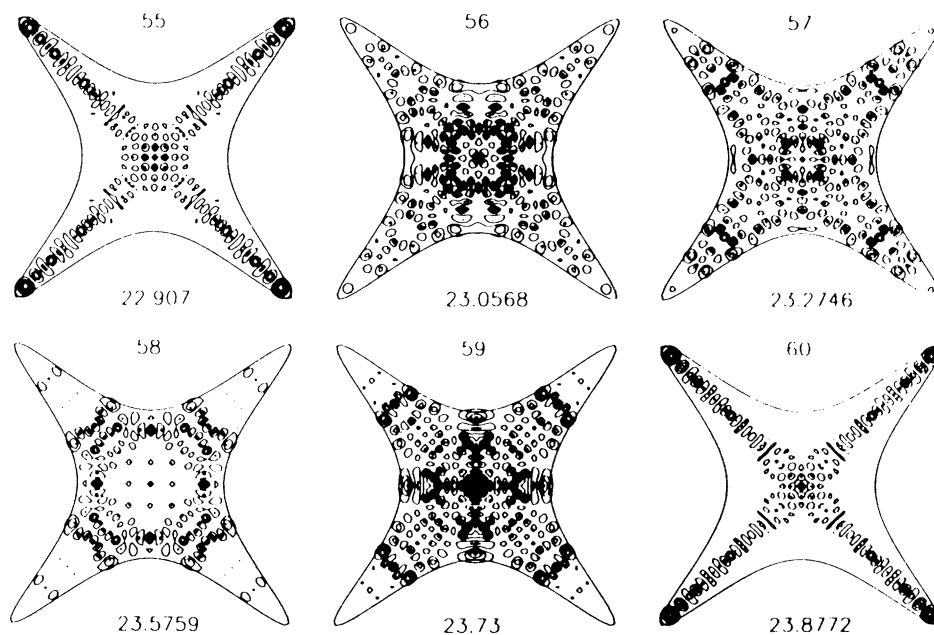


Figure 2. Quantum states of the quartic oscillator. Quantum energies of each eigenstate are in reduced units ($E_0 = 0.5$, see text). Only A_1 symmetry states are shown. A more complete set of figures of eigenstates may be found in Eckhardt *et al.* (1989).

To answer these questions Eckhardt *et al.* (1989) have studied in some detail the classical and quantum dynamics of the following model quartic oscillator system. The two degree of freedom hamiltonian is

$$H = \frac{1}{2}(p_x^2 + p_y^2) + x^2y^2 + \frac{1}{4}\beta(x^4 + y^4), \quad (4)$$

where the parameter $\beta = 0.01$. With this choice, the classical dynamics are chaotic, all periodic orbits we find are unstable in the Liapunov sense. This hamiltonian has an important simplifying feature, because of the homogeneity of the kinetic and potential terms, the classical dynamics scale according to the energy. It suffices therefore to study the classical dynamics at only one energy, taken arbitrarily as $E_0 = 0.5$. One finds that the action $S(\epsilon)$ scales linearly with the reduced energy ϵ :

$$S(\epsilon) = S(0) \cdot \epsilon, \quad \epsilon \equiv (E/E_0)^{\frac{3}{2}}. \quad (5)$$

The quantum eigenstates of this hamiltonian may be classified according to the symmetry classes of the C_{4v} group. In figure 2 we show some typical configuration space plots for higher lying states with A_1 symmetry. One immediately notes that

Phil. Trans. R. Soc. Lond A (1990)

states 55 and 60 are scarred along the channels. Each channel supports a straight line periodic orbit so that again we have found an example of scars along unstable orbits.

A systematic study of the periodic orbits of this system showed that there are many periodic orbits that are localized around the central channel orbit, an example of one of these is shown in figure 4*a*. These orbits seemed to us to be the remnants of broken KAM curves (Lichtenberg & Lieberman 1983) and so we used them to obtain an approximate adiabatic hamiltonian in a novel way which stresses the fact that the scars are not related to a single periodic orbit, but rather to a family of orbits. Suppose that in fact the channel orbit were stable so that motion around it were integrable. This would imply the existence of an adiabatic hamiltonian h_{ad} such that $h_{\text{ad}}(S_{\parallel}, S_{\perp}) = \epsilon$. Thus an adiabatic approximation implies a functional relation between two independent action variables denoted S_{\parallel} and S_{\perp} where parallel and perpendicular denotes the directions relative to the channel orbit. To obtain this functional relation we decomposed the actions of all periodic orbits into their parallel and perpendicular components and plotted each orbit as a point in the S_{\parallel}, S_{\perp} plane as shown in figure 3.

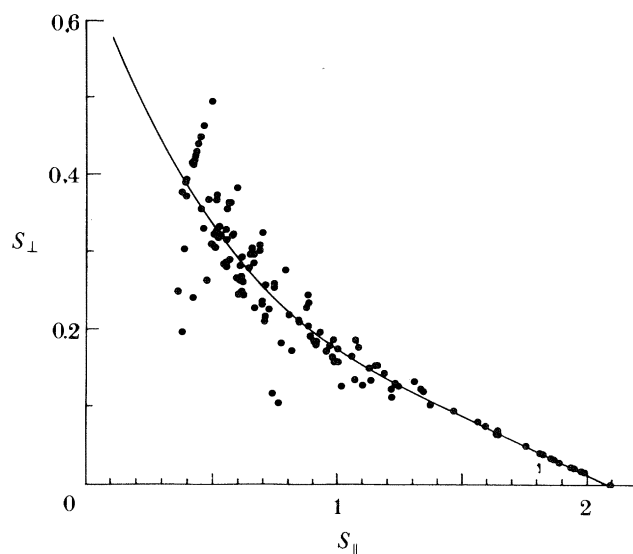


Figure 3. An effective adiabatic hamiltonian for the quartic oscillator, derived by the adiabatic breakup of all computed periodic orbits. The solid line is a least squares fit. For further details, see text and Eckhardt *et al.* (1989).

Since the scatter in the points in figure 3 is not very large, especially in the region where $S_{\parallel} \gg S_{\perp}$, one can fit a curve using a least squares criterion and then use this curve to derive the adiabatic hamiltonian. This integrable hamiltonian is then quantized using the usual EBK quantization conditions, that is $S_{\parallel} = (m + \frac{1}{2})\hbar$ and $S_{\perp} = (n + \frac{1}{2})\hbar$, where n, m are integers. The agreement obtained in this way is good, for example, the adiabatic approximation for the energies of states 55 and 60 shown in figure 2 is (in reduced energy units) 22.948 and 23.908 respectively, while the exact quantum energies are 22.907 and 23.875 respectively. The average spacing between quantum levels in this range is 0.2, much larger than the error in the prediction of the individual eigenstates.

Phil. Trans. R. Soc. Lond A (1990)

Beyond the good agreement, this method has the added advantage over standard adiabatic breakups (Chang 1984; Martens *et al.* 1989) in that it predicts also when the adiabatic approximation can no longer be used to assign single eigenstates. The (scaled) energy dependence of the classical density states is $\rho = 2\epsilon$. At $\epsilon = 20$ the mean spacing between quantum levels is therefore 0.025, taking the quantum symmetry into consideration leads to a mean spacing of $8 \times 0.025 = 0.2$ for a given symmetry subgroup. From the standard deviation of the fit one can estimate whether the uncertainty in the resulting quantized energy is greater or less than the mean level spacing. If less, then the adiabatic hamiltonian is meaningful and can be used to predict and assign single quantum states even though the classical dynamics are chaotic.

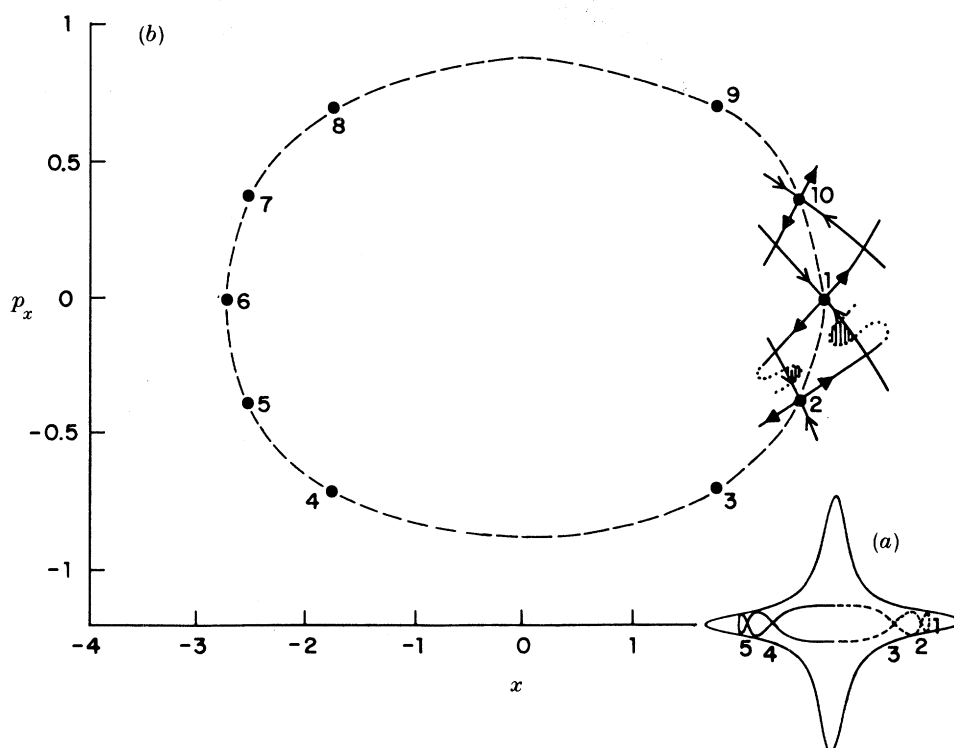


Figure 4. Approximate KAM curves constructed from stable and unstable manifolds of an unstable periodic orbit. The orbit is shown as an inset in panel (a). Panel (b) shows a surface of section of the orbit ($y = 0, p_y > 0$) and its time reverse (filled circles). The heavy lines are the computed (B. Eckhardt, unpublished results) stable and unstable manifolds of the two orbits. The dotted line and shaded area are schematic representations of the turnstiles formed after iteration of one period. For further details, see text.

This method provides an internally consistent estimate for the breakdown of the adiabatic approximation; however, it still suffers from one major defect, the coordinate system chosen – parallel and perpendicular to the channel orbit – is still arbitrary. We have not demonstrated that this is the best possible adiabatic breakup. A remedy for this deficiency is proposed in the next section.

(b) *Semiclassical quantization of unstable periodic orbits*

The main idea underlying the quantization method described below is that one should use the classical dynamics themselves to identify the best possible adiabatic breakup. Before going to the general case, it is useful to study again the quartic oscillator. In figure 4*a* I plot the configuration space path of a typical periodic orbit which is localized around the channel orbit. The solid circles in figure 4*b* show the projection of this orbit and its time reverse on a surface of section. The dashed line connecting the solid circles is arbitrary, but is meant to convey the impression that the pair of orbits may be thought of as lying on a broken KAM curve. The adiabatic approximation presented in the previous subsection really consists of constructing such an arbitrary line. Here I propose instead that one should use the stable and unstable manifolds of the orbit (Lichtenberg & Lieberman 1983) and their intersections to construct the optimal adiabatic approximation for this orbit.

Consider the solid circles denoted 1, 2 in figure 4*b* and their stable and unstable manifolds, (denoted by the heavy arrows). The intersection of the stable and unstable manifolds of the two points forms a quadrilateral object whose mirror image (obtained by reflection about $p_x = 0$) is a quadrilateral joining points 10 and 1. Integrating all points on the pair of quadrilaterals (one iteration) until they come back to the surface of section for the first time, will move them so that they will connect points, 3, 4 and 2, 3 respectively. Three further iterations will move the quadrilaterals so that they adjoin points 9, 10 and 8, 9 respectively. In this manner, for this specific orbit, four iterations will lead to two approximate KAM curves, an inner curve enclosing an area $S_1^<$ composed of the inner boundary of the quadrilaterals and an outer curve enclosing an area $S_1^>$ composed of the outer boundaries of the quadrilaterals. Flux conservation assures us that the area enclosed by each of the ten quadrilaterals is identical.

A trajectory initiated within the region of the first quadrilateral, cannot escape from the phase space bounded between the two approximate KAM curves before one period (T) of the periodic orbit. Only after a fifth iteration, which will map the quadrilateral between points 9, 10 back to a quadrilateral between points 1, 2, will such a trajectory be able to escape. The probability of escape may be defined (Mackay *et al.* 1984; Bensimon & Kadanoff 1984) as the ratio of the area of the two turnstiles (hatched region in figure 4*b*) formed by the fifth iteration and the area enclosed between the two broken KAM curves.

Thus far, there is nothing unique to this construction. Any arbitrary quadrilateral object connecting points 1 and 2, would have the same properties. The reason for using the stable and unstable manifolds to construct the approximate KAM curves is in fact that of all possible quadrilaterals with the same area, the minimum escape probability will be found for those constructed from the stable and unstable manifolds (Bensimon & Kadanoff 1984). Thus, the present construction maximizes the average time that a trajectory will spend with action between $S_1^<$ and $S_1^>$.

One can repeat the same process, with the same orbit but on the surface of section corresponding to the second degree of freedom. This will lead to the second pair of 'action variables' $S_2^<$ and $S_2^>$. We define an average action for each degree of freedom $\langle S^i \rangle$ and an action uncertainty ΔS_i as

$$\langle S_i \rangle \equiv \frac{1}{2}(S_i^< + S_i^>), \quad \Delta S_i \equiv S_i^> - S_i^<, \quad i = 1, 2. \quad (6)$$

It is possible to repeat this process for all periodic orbits up to a given time length,

plot the two action variables and their uncertainties just as done in figure 3 and extract the optimal adiabatic hamiltonian, which is then quantized with the usual EBK prescription. The uncertainties in the actions will lead to an uncertainty in the semiclassical energy, which may, however, still be smaller than the mean level spacing. In this case, one will be able to assign individual quantum states in terms of the adiabatic approximation and these states will localize in phase space around the approximate EBK curves leading to the phenomenon known as scars. In addition, one may evaluate the escape probabilities from the turnstile areas to estimate the validity of the adiabatic approximation.

5. Discussion

The main result presented in this paper is that one can use periodic orbits and their stability frequencies to assign experimental coarse grained spectra of small molecular systems at high energies. Even when the classical dynamics are chaotic, we have demonstrated for some very different systems that one will still find quantum states that are localized around certain families of periodic orbits and which can be assigned in terms of the periodic orbit normal modes. These scars were found in realistic three-dimensional systems, which include both scattering resonances as in the hydrogen exchange reaction as well as high-energy states in strongly bound molecules such as H_3^+ . This localization leads to increased spectral intensities for the localized states (Sepulveda *et al.* 1990), and so they will be reflected as peaks in a coarse grained absorption or SEP spectrum.

The mechanism leading to this localization is the short time stability of classical trajectories in the vicinity of an adiabatically stable periodic orbit. This short-time stability can be quantified in terms of an adiabatic hamiltonian, which when quantized semiclassically leads to good agreement with exact quantal energies of states localized around the orbit. A general methodology for construction of adiabatic hamiltonians has been proposed. The method stresses the short time nature of the localizations and uses known results in nonlinear dynamics to estimate the validity of the adiabatic approximation. In this way, one can predict whether a family of periodic orbits will actually lead to quantum scars.

This adiabatic quantization method, which relies on intersections of stable and unstable manifolds of unstable periodic orbits, may also be applied to cases where a central orbit (such as the hyperspherical orbit in ABA scattering) is stable but the regular regions of phase space surrounding it is too small for standard EBK quantization. Outside the regular region, one will find unstable orbits whose stable and unstable manifolds can be used to construct approximate KAM curves. In this way one will be able to obtain anharmonic corrections for states with excitations perpendicular to the central orbit.

The main drawback of the adiabatic quantization method is that it is limited to two degree of freedom systems. It is not clear how one can efficiently generalize the method to three or more degrees of freedom. However, the periodic orbit normal mode approximation is easily applied to many dimensional systems so that we expect the linear stability analysis of periodic orbits to be a powerful practical tool for assignment of experimental high-energy coarse-grained spectra.

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Periodic orbit assignment

359

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