Classical-quantum correspondence and the analysis of highly-excited states: periodic orbits, rational tori and beyond

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Abstract

In this chapter we survey recent results on the application of semi-classical periodic theory to analyze highly excited states of atoms and molecules. We discuss a model Hamiltonian for doubly-excited states of the helium atom, quartic oscillators coupled by a quartic interaction term, Morse oscillator Hamiltonians describing a pair of coupled molecular vibrations, and a 3-mode Hamiltonian for the vibrational modes of H$_2$O. Our focus is on new insights into dynamics obtained by extracting information on underlying classical phase space structure directly from quantum spectra.

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1 Introduction and motivation

Study of the “classical-quantum correspondence” covers a wide range of topics, as exemplified by the articles in this Volume. One can, for example, compare directly the results of quasiclassical trajectory calculations and quantum scattering calculations of suitably averaged vibrational energy transfer probabilities for the same system [1]. One can also attempt to rationalize the shapes of eigenstates in strongly coupled systems in terms of scarring [2] by classical periodic orbits [3]. In the work to be discussed here, we seek to establish quantitative connections between the quantum mechanical properties (level spectrum, wavefunctions) of a Hamiltonian of physical interest and the classical mechanics (regular, chaotic, mixed phase space [4, 5]) of the corresponding $\hbar \to 0$ limit classical system.

Our key tool is semiclassical periodic orbit (po) theory [5]. This approach to the study of the classical-quantum correspondence has been the focus of an enormous amount of effort in the past 20 years or so. (For reviews of earlier work on this and related subjects, see [6].) Many studies on systems with two degrees of freedom (dof) have established the role of classical periodic orbits in providing an essential connection between classical and quantum mechanics [6]. Systems with $N \geq 3$ dof have not yet been extensively studied [7].

Our particular focus here is on the classical-quantum correspondence for molecular vibration Hamiltonians. As is well-known, the nature of highly-excited vibrational and rotation-vibration states of polyatomic molecules is a long-standing problem of central importance in chemical physics [8]. On the one hand, we seek ways to extend the methods of traditional spectroscopy to assign “good” quantum numbers to states in cases where strong couplings between states and resultant intramolecular vibrational energy redistribution [9] have rendered the standard picture of weakly interacting normal mode vibrations and quasi-rigid rotor states invalid [10]. On the other hand, the breakdown of assignability signals the onset of the “statistical” behavior posited by traditional theories of reaction rates [11]. It is clear that molecular spectra provide important laboratories for investigating the fundamental problem of the influence of non-regular classical dynamics on few-body quantum systems.

The fundamental aim of molecular spectroscopy is to derive information about the a priori unknown molecular Hamiltonian $\hat{H}$ and its associated dynamics. The spectroscopic Hamiltonian is traditionally determined by iterative fitting of parameters in a model Hamiltonian $\hat{H}(\alpha)$ [10], perhaps derived in a systematic fashion from the fundamental Eckart Hamiltonian via perturbation theory [12]. Once $\hat{H}$ has been determined, the quantum dynamics of nonstationary states can then be investigated [13].

Our understanding of the quantum dynamics of $\hat{H}$ is however greatly enhanced by study of the corresponding classical Hamiltonian $\mathcal{H}$. At the most elementary level, chemists continue to picture molecules as mechanical “ball-and-spring” objects, while the trajectories of ball bearings rolling on potential surfaces have long served to illustrate the qualitative influence of potential energy surface shape upon reactive dynamics [8, 14].
It is therefore important to develop methods for analysis of molecular spectra that are (as far as is possible) rooted firmly in the underlying classical mechanics of the molecular Hamiltonian; here, semiclassical methods, especially semiclassical period orbit theory, provide an essential bridge between the classical and quantum aspects of the problem [15]. Ideally, a method should be capable of processing data on quantum energies $\{E_j\}$ and line intensities to derive information on the molecular phase space structure (large-scale resonances, existence of conserved or approximately conserved quantities (polyads) [16, 17]), and the changes in phase space structure with energy $E$ and total angular momentum $J$. Even inherently “quantum” phenomena such as tunneling splittings in high-resolution rotation-vibration spectra can be related to underlying classical phase space structure [18].

Several novel approaches to the analysis of molecular spectra have recently been proposed that exploit the classical-quantum correspondence to provide insight into the intramolecular dynamics underlying the spectrum. Without discussing them in any detail, we mention several that are more or less closely related to the work to be discussed here: statistical Fourier transform spectroscopy [19]; bifurcation theory and catastrophe maps [20]; stratified Morse theory [21]; hierarchical tree models [22]; rotational energy surfaces [23]; classical trajectory approaches [24]; semiclassical approaches involving “cellular dynamics” using the Van-Vleck propagator $K_{sc}(x, x', t)$ [25]; local random matrix models and scaling approaches [26, 27].

In the present article we describe two approaches to the analysis of spectra that have been the focus of our recent research. The first approach, energy-time $(E, \tau)$ (or so-called “vibrogram”) analysis of spectra, has recently been developed by us [28, 29] and others [30, 31, 32], and builds upon early work on the application of semiclassical periodic orbit theory to nonscaling systems such as molecular Hamiltonians [33, 34]. The second approach applies Chirikov resonance analysis [35] to assign eigenstates of multimode systems via the quantum-classical correspondence [36, 37]. This work builds on the pioneering application of resonance analysis to molecular Hamiltonians by Oxtoby and Rice [38] (see also [39, 40]), and is related to recent work by Kellman and coworkers [41].

In section II we provide a brief overview of semiclassical periodic orbit theory, outlining difficulties associated with application to molecular vibrational Hamiltonians. Applications to doubly-excited states of two-electron atoms and to coupled quartic oscillators are reviewed. We then introduce the essential idea of energy windowing that underlies the energy-time analysis of molecular spectra. Applications of energy-time analysis to some model molecular vibrational Hamiltonians are given in section III. In section IV we briefly turn to the application of Chirikov resonance analysis to multimode vibrational Hamiltonians. Applications to the Baggot Hamiltonian for H$_2$O are discussed; we consider the problem of assigning eigenstates in the presence of strong intermode coupling.
2 Semiclassical periodic orbit theory

2.1 General background

Semiclassical periodic orbit theory provides an essential link between the classical mechanics and the quantum spectrum of a given Hamiltonian, the so-called trace formula for the density of states \( [5] \). In the simplest (primitive semiclassical) form of the theory, the density of states \( \rho(E) = \sum_i \delta(E - E_i) \) is expressed as the sum of two parts: a smooth term (the Thomas-Fermi density), and an infinite sum of oscillatory contributions from individual classical periodic orbits, as \( \hbar \to 0 \):

\[
\rho(E) \sim \bar{\rho}(E) + \sum_p \sum_k A_{pk}(E) \cos \left[ \frac{2\pi k S_{pk}(E)}{\hbar} + \phi_{pk} \right].
\] (1)

Here the subscript \( p \) specifies the po and the index \( k \) labels its \( k \)-th repetition. The quantity \( \bar{\rho}(E) \) is the mean level density, and is a smooth function of the energy \( E \). The oscillatory part of the density of states is then a sum of contributions from all pos \( p \). The quantity \( S_{pk} \) in the exponent is the action of \( p \). The precise form of the amplitude \( A_{pk} \) depends on the nature of the system phase space in the vicinity of \( p \), while \( \phi_{pk} \) is a phase whose precise definition is unimportant for present purposes. Both \( S_{pk} \) and \( A_{pk} \) depend on the energy \( E \) in general.

The semiclassical expression for the unweighted density of states can be generalized to spectra weighted by overlap with a sufficiently smooth wavepacket state \( [42] \).

In so-called harshly chaotic systems, all periodic orbits are isolated and unstable \( [5] \). The appropriate version of the trace formula is then that originally applied by Gutzwiller to the anisotropic Kepler problem \( [5] \). For completely integrable systems, on the other hand, all trajectories lie on invariant tori \( [4] \), and almost all periodic orbits appear in continuous families lying on rational tori whose independent frequencies of motion are commensurable. The appropriate version of the trace formula in this case is due to Berry and Tabor (BT) \( [43] \), who derived their result from the spectrum obtained by EBK quantization \( [5] \). The BT version of the trace formula will be the starting point for our analysis of the spectra of molecular vibrational Hamiltonians weakly perturbed from the integrable limit. The contribution to the density of states from a stable po as given by Gutzwiller’s formula was shown by Miller to be an approximation to the EBK density of states for tori in the vicinity of the given po \( [44] \).

It is important to emphasize the different \( \hbar \) dependence of the contributions to the density of states of isolated versus families of periodic orbits on rational tori. In a 2 dof system, the amplitude \( A_p \propto \hbar^{-1} \) for an isolated po (stable or unstable), whereas the amplitude for a 1D family of pos on a rational 2-torus \( \propto \hbar^{-3/2} \), i.e., the latter is more singular in the semiclassical limit.

At or near bifurcations of periodic orbits, one typically has clusters of orbits whose contribution to the semiclassical density of states must be treated collectively, rather than separately. For example, primitive semiclassical Gutzwiller
amplitudes $A_{p_k}$ diverge at po bifurcations [5]. The required uniform semiclassical theory [45] has been developed by a number of workers [46, 47, 48], starting with the important work of Ozorio de Almeida and Hannay [46]. We note in particular that, in the case of the breakup of a rational torus into an island chain, Ozorio de Almeida has derived a uniform semiclassical formula that interpolates between the BT contribution of the rational torus and the sum of contributions from the isolated stable/unstable Poincaré-Birkhoff pair as given by the Gutzwiller formula [47].

For mixed systems, in which regular and chaotic regions of phase space are interwoven in a very complicated and as yet not fully understood fashion [49], there is no rigorous semiclassical trace formula; rather, one assumes that the connection between the quantum density of states and the underlying classical phase space structure can be understood, in a coarse-grained sense at least, by considering the semiclassical density of states as a direct sum of contributions from regular regions (BT) and chaotic regions (Gutzwiller), with uniform corrections as needed.

Although the semiclassical po expressions for the quantum level density can in principle be used in the “forward” mode to compute semiclassical eigenvalues for individual levels, in practice there are many difficult issues concerning enumeration of pos and convergence, especially for systems with mixed phase space structure such as molecular Hamiltonians [6]. In the work to be described below, we use po theory “in reverse” to extract information on classical phase space structure directly from vibrational eigenvalues, and so avoid fundamental convergence issues. The connection between fluctuations of the quantum density of states about the Thomas-Fermi value is revealed by Fourier analysis of the quantum spectrum, whose power spectrum exhibits peaks at multiples of the periods (or actions) of the least unstable pos.

### 2.2 Scaling systems

In scaling systems, the potential energy is a homogeneous function of the coordinates. In such systems, the classical phase space structure is essentially independent of the energy, and po properties such as period, action and stability all scale in a known way with $E$ [50].

For example, if $V(q) \propto q^\nu$, then

\begin{align}
    p(\tau) &= \left( \frac{E}{E_0} \right)^{1/2} p_0(t), \\
    q(\tau) &= \left( \frac{E}{E_0} \right)^{1/\nu} q_0(t), \\
    \tau &= \left( \frac{E}{E_0} \right)^{(2-\nu)/(2\nu)} t, \\
    S(E) &= \varepsilon S(E_0),
\end{align}

\Halmos
where the scaled energy \( \varepsilon \equiv (E/E_0)^{(v+2)/2v} \). The scaling property greatly simplifies semiclassical po analysis, as the modified density of states \( \tilde{\rho} \) can be written in terms of \( \varepsilon \)

\[
\tilde{\rho}(\varepsilon) \sim \tilde{\rho} + \sum_{p,k} \tilde{A}_{pk} \cos \left[ \varepsilon k S(E_0) / \hbar \right],
\]

(6)

where \( \tilde{A}_{pk} \) and \( S(E_0) \) are independent of \( \varepsilon \).

For scaling systems, it is then possible to use the whole available level spectrum to derive information on the underlying classical mechanics; Fourier analysis of the modified density of states will yield peaks at actions \( S_k(E_0) \) corresponding to po \( k \) at reference energy \( E_0 \). The larger the available range of energy spectrum, the sharper the peaks in the power spectrum, hence the more precisely determined the classical actions.

Semiclassical po analysis has been applied to many scaling systems following the important work of Wintgen [51]; here, we consider briefly two examples from our own research: the collinear Helium atom [52, 53] and coupled quartic oscillators [54, 55].

**PO analysis of Helium atom**

The properties of doubly-excited autoionizing resonances of two-electron systems such as He and H\(^-\) have been the subject of intense theoretical interest for over 30 years, ever since the first experimental indications of the complete breakdown of the independent-particle picture due to electron correlation [56]. Much effort has been devoted to seeking new quantum numbers to describe the highly correlated motion in such “planetary atoms” [56].

On general correspondence principle grounds, planetary atoms would appear to be good candidates for semiclassical analysis due to the large quantum numbers involved [57]. The problem of semiclassical quantization of multielectron systems was however left unsolved in the Old Quantum Theory [58], and it is only recently that new insights into the classical mechanics of chaotic systems and the classical-quantum correspondence (in particular, po theory) have enabled renewed progress to made. Our work [52, 53] and that of others [59, 60] has shown that modern semiclassical methods are able to provide novel insights into the dynamics of the correlated electron pair in doubly-excited states of 2-electron systems.

Our efforts were directed towards the study of the highly-excited states of a collinear, two degree-of-freedom model for the Helium atom. This Hamiltonian describes two electrons in the field of an infinitely heavy nucleus of charge \( Z \), where \( 0 \leq r_1, r_2 \leq \infty \):

\[
H = \frac{p_{r_1}^2}{2} + \frac{p_{r_2}^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_1 + r_2}.
\]

(7)

Only the radial (stretching) degrees of freedom are included. The relative angular (bending) motion is suppressed (\( \theta_{12} = \pi \)), and the total angular momentum set equal to zero.
Periodic orbit analysis

Classical Coulomb Hamiltonians describing are homogeneous of degree \(-1\) in the coordinates, and actions and stability properties of classical periodic orbits (pos) need only be computed at a single energy \((E_0 = -1, \text{ say})\), greatly simplifying the classical mechanical aspect of the calculation. For \(E < 0\), the classical collinear He atom is highly chaotic, with no bound quasiperiodic trajectories (invariant tori) or stable pos \([59]\). There exists however a measure zero set of bound trajectories, composed of isolated unstable pos, associated homoclinic and heteroclinic orbits, and bound aperiodic orbits. In fact, empirical evidence suggests the existence of a complete binary symbolic code for pos that neither begin nor end in triple collision \([52, 53, 59]\). The po associated with the famous Wannier ridge \([61]\) is the “symmetric stretch” orbit with \(r_1(t) = r_2(t)\), and begins and ends in triple collision \((r_1, r_2 \to 0)\). The nonregularizability of the triple collision means that the symmetric stretch is effectively infinitely unstable \([62]\).

The positions of highly excited quasibound doubly-excited states of collinear He (Hamiltonian Eq. (2.4)) were computed using the stabilization method \([63]\). The Hamiltonian (2.4) was diagonalized in a fixed size spatially symmetric (singlet) direct product basis of two-electron functions formed from a complete denumerable set of single-particle states depending on a scale parameter. The smoothed density of quasibound doubly-excited states was then obtained by projecting computed eigenvalues for a range of scaling parameter onto the energy axis \([52]\). Fig. 1 shows the density of resonances for an energy range corresponding roughly to doubly excited states \((n, n' = n)\) with principal quantum number \(n\) ranging from 20 to 45 (for each electron) \([52]\).

The power spectrum of the density of states of Fig. 1 obtained by Fourier transformation with respect to the scaled energy \(\varepsilon = (E)^{\frac{1}{2}}\) is shown in Fig. 2, and consists of a series of sharp peaks, each of which can be assigned to at least one classical po.

These results show unambiguously that the most prominent peaks in the power spectrum are associated with pos of symmetric stretch character, for example, the “hyperangular” po \([59]\) with action \(S/\hbar = 1.83\). Most notably, there is no peak at the action of the Wannier mode \((S/\hbar = 2 \times (Z - 0.25) = 3.50)\). There is therefore no evidence for sequences of doubly-excited levels described by quantization of the Wannier ridge motion \([64]\). Recalling that, according to primitive semiclassical po theory, the amplitude of the contribution from an unstable po to the density of states decreases exponentially with the instability exponent, the absence of a peak associated with the Wannier mode can be understood after the fact in terms of its extreme instability.

Localization of doubly-excited wavefunctions in the vicinity of periodic orbits of asymmetric character was found for the collinear He model \([52]\) and for near-collinear states of the 3D \(L = 0\) He atom \([52, 59]\). Moreover, using only contributions from asymmetric stretch pos, Wintgen et al. were able to apply the so-called cycle expansion resummation of the trace formula to compute accurate semiclassical eigenvalues for near-collinear states of He**, thereby solving the long-standing problem of semiclassical quantization of two-electron systems \([53, 59]\).
The new insights into the nature of the electron pair motion in He** derived from semiclassical po theory pose severe difficulties for the large body of classical, quantum and semiclassical theory on the nature of doubly-excited states based on the “Wannier picture” carried out over the last 30 years or so [64].

Quartic oscillators

Two degree of freedom systems with homogeneous quartic potentials have been widely studied [65, 66, 67, 68, 69, 70, 71, 72, 73, 74]. Early classical investigations of the $x^2y^2$ potential suggested that the system was completely (harshly) chaotic [65]; subsequent studies have shown the existence of small stable regions in phase space [70, 71]. Wavefunction localization or ‘scarring’ in configuration space [67] and in phase space [69, 74] have been examined, and approximate adiabatic quantization schemes proposed for eigenvalues [67, 73]. A detailed study of coupled quartic oscillators has been made by Bohigas, Tomsovic and Ullmo [72]. Among other aspects, these authors have investigated the relation between classical phase space transport (flux through partial barriers) and quantum features such as energy level spacing statistics.

In our work we studied the classical-quantum correspondence for a system of two quartic oscillators with quartic potential coupling [54, 55]:

$$V(x, y) = \eta_1 q_1^4 + \eta_2 q_2^4 + \gamma q_1^2 q_2^2.$$ (8)

Real molecular vibrational Hamiltonians typically exhibit mixed phase space structure: in terms of the quartic potential model, they lie somewhere between the integrable limit $\gamma = 0$, where the density of states is given by the Berry-Tabor sum over resonant tori [43] (see Fig. 3), and the almost completely chaotic limit $\gamma \to \infty$, where the Gutzwiller formula for ‘hard’ chaos applies. In order to study the passage between these two limits, we computed the quantum density of states over large energy ranges and for many values of the coupling parameter $\gamma$ [55]. By examining periodic orbit spectra at a number of coupling parameter values one can follow in some detail the effects of periodic orbit bifurcations on the quantum spectrum (see Figure 4).

An important bifurcation in the coupled quartic oscillator system is the symmetric isochronous or pitchfork bifurcation of the primary oscillator modes (Figure 5). Following the approach of Ozorio de Almeida and Hannay [46] and Ozorio de Almeida and Aguiar [48], we derived a uniform semiclassical expression for the contribution to the density of states from the set of orbits involved in the bifurcation [54]. The quantitative accuracy of the theory can be gauged from the comparison of analytical and numerical results shown in Figure 6.

2.3 Nonscaling systems: molecular Hamiltonians

General comments

In the spectroscopy of excited vibrational states of molecules, the objects of prime interest are either the unweighted density of states $\rho(E)$ or the overlap
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spectrum $I(E)$, where

$$I(E) = \sum_j |\langle \phi | \psi_j \rangle|^2 \delta(E - E_j),$$

(9)

$|\psi_j\rangle$ is the $j$th vibrational eigenstate, and $|\phi\rangle$ is a localized state (for example, a Gaussian wavepacket) displaced from the equilibrium configuration [75]. The overlap spectrum is just the Fourier transform of the wavepacket autocorrelation function $\langle \phi(0) | \phi(t) \rangle$ [24, 75].

It is intuitively reasonable that classical motions leading to recurrences of the initial wavepacket will determine in some fashion the detailed structure seen in a vibrational spectrum. Tomovic and Heller have analyzed $\langle \phi(0) | \phi(t) \rangle$ semiclassically in terms of biasymptotic (homoclinic and heteroclinic) orbits [76]. Extension of the trace formula to the matrix elements of smooth operators [42] (in this case, the density operator corresponding to the initial Gaussian state) provides a secure foundation for quantitative analysis of vibrational spectra in terms of strictly periodic orbits.

Nonscaling systems and energy windowing

Molecular vibrational Hamiltonians are prototypical examples of nonscaling systems. The vibrational phase space structure can change dramatically with energy, and the evolution of classical phase space structure with energy is of considerable interest. Many previous applications of semiclassical po theory to molecular spectra have mainly addressed qualitative issues of wavefunction localization [3]. (Periodic orbits and their bifurcations also form the basis of Kellman’s approach to the analysis of resonantly coupled modes, in which a systematic study is made of bifurcations on the polyad phase sphere [20].)

To obtain information on the classical dynamics from the quantum spectrum of a nonscaling system, it is necessary to analyze the density of states in the vicinity of a particular energy value $E$. One obvious possibility is to multiply the density of states by a suitable window function centered at $E$. The use of window functions is familiar in the analysis of nonstationary signals in the time domain [77]. In our own work, for example, local frequency analysis of irregular trajectories has provided considerable insight into pathways for exploration of phase space in multimode systems [78] (see also [79]). Use of a window function enables one to explore the evolution of po periods with energy using quantum $(E, \tau)$ plots, and to identify signatures of classical bifurcations.

A windowed Fourier transform of the absorption spectrum of $O_3$ was used by Johnson and Kinsey in their pioneering work to examine the evolution of po periods with energy on the dissociative upper potential energy surface [33]. The window used was a 3-term Blackman-Harris function [77]. Baranger et al. have shown more formally that the Fourier transform of the quantum density of states with respect to $E$ obtained using a Gaussian window centered at some chosen energy $\bar{E}$ contains peaks associated with classical pos at the same chosen energy [34]. Use of a Gaussian window of width $\Delta E$ corresponds to taking the
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Gabor [80] or Husimi [81] transform of the density of states [34]:

\[
G_{\tilde{E}}(t) = \int_{-\infty}^{\infty} \exp \left[ -\frac{(E - \tilde{E})^2}{2\Delta E^2} \right] \exp \left( -\frac{iEt}{\hbar} \right) \text{Tr}[\delta(E - \tilde{H})]dE \\
= \sum_n \exp \left[ -\frac{(E_n - \tilde{E})^2}{2\Delta E^2} \right] \exp \left( -\frac{iE_n t}{\hbar} \right). \tag{10}
\]

The power spectrum is then simply \(|G_{\tilde{E}}(t)|^2\). In the semiclassical limit \(\hbar \to 0\), we can substitute the GTF for the density of states into (10); after expanding the \(E\)-dependent po action about \(\tilde{E}\), noting that the po period

\[
\tau_p = \frac{\partial S_p(E)}{\partial E}, \tag{11}
\]

and ignoring the \(E\)-dependence of the amplitudes \(A_{pk}\), we obtain a power spectrum with peaks centered at the periods \(\tau_p\) of classical pos at the energy \(\tilde{E}\). Computation of the power spectrum \(|G_{\tilde{E}}(t)|^2\) at many values of \(\tilde{E}\) yields an energy versus period \((E, \tau)\) plot, which can be compared with the corresponding classical result [34].

Baranger et al. introduced the use of a Gaussian window, and computed classical and quantum \((E, \tau)\) plots for a number of potentials [34]. We have examined the bifurcation associated with the local to normal mode transition in a system of two 1:1 resonantly coupled anharmonic oscillators [28], and also studied in some detail spectral patterns and dynamical bifurcations in Fermi resonant systems [29]. This work is discussed below.

Other recent work using similar approaches includes the “vibrogram” analysis of Liévin et al. [30] and of Gaspard, Hirai and Heller [31] (see also [32]), the work of Pique and coworkers on CS\(_2\) [83], the work of Joyeux on CO\(_2\) [84], and the work of Main and Taylor [86]. Houle and Henley have applied \((E, \tau)\) analysis to the quantum spectra of coupled spin systems [87]. Similar ideas have also been applied in nuclear physics [88].
3 \((E, \tau)\) analysis of molecular vibrational Hamiltonians

We now discuss several examples of \((E, \tau)\) analysis of molecular vibrational Hamiltonians. There are, broadly speaking, two types of Hamiltonian one can study. The first type is an \(N\)-body Hamiltonian for nuclear motion (usually in the Born-Oppenheimer approximation)

\[
\hat{H} = \frac{\hat{p}^2}{2} + V(q),
\]

where \(V(q)\) is the potential energy surface as a function of nuclear coordinates \(q\). The second type is an effective spectroscopic Hamiltonian of the form (ignoring rotations for simplicity) [10]

\[
\hat{H} = \hat{H}_0(\hat{n}) + \hat{H}'(\hat{a}, \hat{a}^\dagger),
\]

where \(\hat{n}\) is a vector of number operators for a set of zeroth order modes, the zeroth-order Hamiltonian \(\hat{H}_0\) has the form

\[
\hat{H}_0 = \sum_k h \omega_k (\hat{n}_k + \frac{1}{2}) + \sum_{k,k'} X_{k,k'} (\hat{n}_k + \frac{1}{2})(\hat{n}_{k'} + \frac{1}{2}) + \ldots
\]

and \(\hat{H}'\) is a nonlinear, nonseparable perturbation written as a sum of \(m:n\) resonant coupling terms of the form

\[
H^{m:n} = c_{m:n} (\prod_k \hat{a}_{k}^{m_k} (\hat{a}_{k}^{\dagger} n_k + c.c.).
\]

An example of a model spectroscopic Hamiltonian is the Baggot vibrational Hamiltonian for \(H_2O\) [89]. This is a three degree of freedom local mode Hamiltonian which includes two 2:1 stretch-bend resonant terms \(H^{2:1,1}\), \(\sigma = 1\) or 2, a 1:1 stretch-stretch resonant term \(H^{1:1}\) and a 2:2 stretch-stretch term \(H^{2:2}\):

\[
H = H_0 + H^{1:1} + H^{2:2} + \sum_{\sigma=1,2} H^{2:1}_{\sigma},
\]

where \(H_0\) is the zeroth order Hamiltonian

\[
H_0 = \Omega_s \sum_{\sigma=1,2} I_\sigma + \Omega_b I_b + \alpha_s \sum_{\sigma=1,2} I_\sigma^2 + \alpha_b I_b^2 + \epsilon_{ss} I_1 I_2 + \epsilon_{sb} I_b \sum_{\sigma=1,2} I_\sigma,
\]

and the resonant interaction terms are (in the classical limit)

\[
H^{1:1} = \beta'_{12} (I_1 I_2)^{1/2} \cos(\theta_1 - \theta_2),
\]

\[
H^{2:2} = \beta_{22} I_1 I_2 \cos[2(\theta_1 - \theta_2)],
\]

\[
H^{2:1}_{\sigma} = \beta_{sb} (I_\sigma I_b)^{1/2} \cos(\theta_\sigma - 2\theta_b).
\]
Here, \( \{I_s, \theta_s\}, I_b, \theta_b \) \( \equiv (\mathbf{I}, \theta) \) are canonical action-angle variables for the two local mode stretches and the bend mode, respectively. The Baggot Hamiltonian has a constant of the motion in addition to the energy, the so-called polyad number:

\[
P = I_1 + I_2 + \frac{1}{2} I_b.
\]  

(21)

Use of the spectroscopic Hamiltonian (3.2) has several advantages. First, one can systematically increase the complexity of the Hamiltonian as may be required when fitting levels at higher and higher energies [90]. Second, one can easily build in the conservation of polyad quantum numbers such as \( P \). Third, the mapping between the classical and quantum versions of any such Hamiltonian is readily obtained via the standard correspondence between action-angle variables and creation-annihilation operators:

\[
\hat{a}^\dagger \longleftrightarrow I_1^\frac{1}{2} e^{i\theta}, \quad \hat{a} \longleftrightarrow I_1^\frac{1}{2} e^{-i\theta}.
\]  

(22)

The main disadvantage lies in the fact that the connection between the parameters appearing in the spectroscopic Hamiltonian and the form of the molecular potential surface \( V(q) \) is not a direct one [91]. Our discussion of \((E, \tau)\) analysis of vibrational spectra will nevertheless be based upon the use of model spectroscopic Hamiltonians (3.2).

### 3.1 Harmonic oscillator

The simplest possible vibrational Hamiltonian consists of a set of uncoupled harmonic oscillators. Classically, the Hamiltonian is:

\[
H_0 = \sum_j \Omega_0(j) I_j.
\]  

(23)

For this system, the classical frequencies \( \{\Omega_0(j)\} \) and periods \( \{\tau_0(j) = 2\pi/\Omega_0(j)\} \) are independent of energy, so that the classical \((E, \tau)\) plot consists of a series of vertical lines. Determination of the classical periods from the quantum spectrum is then equivalent to a conventional normal mode analysis, which determines the harmonic normal mode frequencies. (In fact, there are technical difficulties in the derivation of the relevant semiclassical Berry-Tabor formula in the case of harmonic oscillators due to lack of anharmonicity; a uniform semiclassical analysis is required [43].)

### 3.2 1D Morse oscillator

A simple spectroscopically relevant oscillator exhibiting nontrivial dependence of period on energy is the Morse oscillator. The classical Hamiltonian for a 1D Morse oscillator is

\[
H_0(I) = \Omega I + \alpha I^2,
\]  

(24)

with \( \alpha < 0 \). The classical frequency \( \omega(I) \equiv \partial H_0/\partial I \) is then

\[
\omega = \Omega + 2\alpha I = \sqrt{\Omega^2 + 4\alpha E},
\]  

(25)
so that $\omega$ decreases to zero at the dissociation energy $\Omega^2/(4|\alpha|)$.

The 1D Morse oscillator provides a useful test case for the comparison of quantum and classical $(E, \tau)$ plots. The quantum level spectrum is

$$E_n = \hbar \Omega (n + \frac{1}{2}) + \alpha \hbar^2 (n + \frac{1}{2})^2,$$

with $0 \leq n \leq n_{\text{max}}$, $n_{\text{max}} = \text{Int}[(\Omega/2|\alpha|)/\hbar]$. The quantum $(E, \tau)$ plot for the case $\Omega = 1, \alpha = -0.03, \hbar = 1/80$, is compared with the corresponding classical plot in Figure 7. The close agreement serves as a check on the validity of our numerics.

## 3.3 2D uncoupled Morse oscillators

We now discuss the classical-quantum correspondence for a system of two uncoupled Morse oscillators. Although an apparently trivial integrable system, the $(E, \tau)$ analysis of the uncoupled Morse case provides the foundation for understanding the classical-quantum correspondence for spectroscopic Hamiltonians obtained by adding various resonant coupling terms.

### Classical mechanics

In terms of canonical variables $(I_1, I_2, \psi_1, \psi_2)$, the Hamiltonian for two uncoupled Morse oscillators is:

$$H_0 = \Omega_1 I_1 + \Omega_2 I_2 + \alpha_1 I_1^2 + \alpha_2 I_2^2.$$ 

This system is a special case of the more general $N$-mode Hamiltonian

$$H_0 = \Omega \cdot I + I \cdot A \cdot I,$$

where $I$ and $\Omega$ are $N$-vectors of actions and harmonic frequencies, respectively, and $A$ is a symmetric matrix of quadratic coefficients, $A = \tilde{A}$. For this Hamiltonian, classical frequencies are

$$\omega = \Omega + 2A \cdot I.$$ 

From the Berry-Tabor formula, we are interested in determining the periods of orbits on rational tori, those for which all $N$ frequencies are commensurate, i.e.,

$$\omega \propto m \equiv mw.$$ 

The period of the po on the rational torus specified by the vector $m$ is the derivative of the po action with respect to energy $E$

$$\tau_m = \frac{\partial S_m}{\partial E},$$
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where the derivative must taken subject to the constraint that the commensurability condition be maintained. Evaluating the derivative we find

$$\tau_m = \left[ \frac{m \cdot A^{-1} \cdot m}{4E + \Omega \cdot A^{-1} \cdot \Omega} \right]^{\frac{1}{2}}.$$  \hspace{1cm} (32)

The above result is a general expression for the period of a po on a rational $N$-torus in an integrable system with terms linear and quadratic in the action. A system of two uncoupled Morse oscillators is clearly a special case. Using this result we can construct a classical $(E, \tau)$ plot for two uncoupled Morse oscillators; this is shown in Figure 8 for $\Omega_1 = 1.0, \Omega_2 = 0.8, \alpha_1 = -0.03, \alpha_2 = -0.02$. In addition to the $(E, \tau)$ traces associated with the rational 2-tori and their repetitions, we also include in Figure 8 the $(E, \tau)$ lines for the two boundary pos having $I_1 = 0$ and $I_2 = 0$, respectively. According to the BT formula, the boundary pos contribute with a strength $\propto \bar{h}^{-1}$, i.e., the same as isolated pos in the Gutzwiller trace formula. In general, the rational torus corresponding to a given commensurability condition $m$ will emerge from one or the other boundary po at a particular energy. At this energy the rational po and the appropriate multiple of the boundary po have the same period. At higher energies, the period $\tau_m$ increases more slowly with $E$ than that of the boundary po.

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The quantum $(E, \tau)$ plot for the 2 uncoupled Morse oscillators is given in Figure 9. Comparison with classical traces in Figure 8 shows an excellent match of the periods. The striking aspect of the plot is the existence of intense "ridges" associated with rational 2-tori; the traces corresponding to the boundary pos have much smaller amplitudes.

3.4 Coupled Morse oscillators

In this subsection we examine the effect of resonant coupling terms on the quantum $(E, \tau)$ representation of the spectrum of the 2-mode Morse system. We first study the effect of a single 1:1 resonant term, then a single 2:1 resonant coupling term, and finally a system where both 1:1 and 2:1 resonant coupling terms are present [92]. In the first two cases, the corresponding classical problem is integrable; only for the case of two coupling terms is there the possibility of classical nonintegrability, and we shall be interested in its manifestations in the $(E, \tau)$ representation.

Single 1:1 resonance coupling term

Consider adding to the uncoupled Morse oscillator $H_0$ the 1:1 resonance coupling term

$$H^{1:1} = 2\beta \sqrt{I_1 I_2} \cos(\psi_1 - \psi_2).$$  \hspace{1cm} (33)

If the two Morse oscillators are identical, then this Hamiltonian is a model for, e.g., the stretching modes of $H_2O$. In that case, the existence of both local and
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**normal** modes has been well studied [95]. For $H = H_0 + H^{1:1}$, the quantity $I_1 + I_2$ is a constant of the motion, so that the problem is classically integrable. Since $H$ is effectively one-dimensional, a global view of the classical phase space structure is obtained by plotting the Poincaré section at fixed $E$ on the surface of a sphere [96]. The classical phase space structure and bifurcation diagrams on the so-called polyad phase sphere have been extensively studied by Kellman and coworkers [97].

The quantum counterpart of the classical Hamiltonian $H$ is easily obtained. In terms of creation and annihilation operators, the 1:1 coupling term $\hat{H}^{1:1}$ is $\beta (\hat{a}_1^{\dagger} \hat{a}_2 + \hat{a}_1 \hat{a}_2^{\dagger})$. The quantum Hamiltonian $\hat{H}$ conserves the total number of quanta ($n_1 + n_2$), so that together with the energy there are two integrals of the motion. Diagonalization of $\hat{H}$ in a basis of number states $|n_1, n_2\rangle$ gives the quantum level spectrum. Because of the integrability of the quantum Hamiltonian, we are able to diagonalize matrices corresponding to each polyad independently (a polyad is defined by a particular value of $P = n_1 + n_2 + 1$). The effective value of $\hbar$ and the density of states at fixed $E$ can be changed by the following scalings:

$$\omega \rightarrow \bar{\omega} = \omega/c, \ a \rightarrow \bar{a} = a/c^2, \ \beta \rightarrow \bar{\beta} = \beta/c, \ \hbar \rightarrow \bar{\hbar}/c. \quad (34)$$

Using the Gabor transform method described above we have constructed $(E, \tau)$ diagrams from the quantum density of states at fixed coupling parameter $\beta$ as well as $\beta$ versus $\tau$ plots for fixed energy $E$ [28].

In Fig. 10 we show a quantum $(E, \tau)$ plot obtained with coupling parameter $\beta = 0.01$, $\Omega_1 = \Omega_2 = 0.5$ and $\alpha_1 = \alpha_2 = -0.001$. For this value of $\beta$, two symmetry related, stable local mode pos coexist with two normal mode pos, one stable and one unstable [28]. The two normal mode pos have similar periods, and the difference between the periods changes slowly with $E$; the associated $(E, \tau)$ traces are essentially parallel over the whole $E$ range of interest. (The range of $\tau$ values shown in Fig. 10 includes the third to the sixth repetitions of the fundamental pos.) Note once again the presence of intense ridges associated with rational tori resulting from resonant bifurcations of the stable local mode pos (the periods of the two local mode pos are identical). The rational tori in Fig. 10 form a sequence with frequency ratios $m + 1 : m = 3:2, 4:3, 5:4, \text{etc.}$ [28].

In addition to the degenerate case with $\Omega_1 = \Omega_2$, we can consider the effect of a 1:1 resonant coupling on the uncoupled Morse system shown in Figure 11. In the unperturbed system, a rational torus with $m:n$ frequency commensurability consists of a 1-parameter family of pos. Under the action of a resonant $m:n$ perturbation, the torus will break up to give the familiar Poincaré-Birkhoff island chain consisting one or more pairs of stable and unstable pos [49]. It is important to note that these pos are **isolated**, and hence contribute to the density of states as $\hbar^{-1}$, rather than $\hbar^{-3/2}$. In the semiclassical limit, then, breakup of the rational torus is accompanied by loss of intensity of the associated peak in the $(E, \tau)$ plot. This loss of intensity is clearly seen in Fig. 11, where the 1:1 and 2:2 $(\equiv 2 \times 1:1)$ peaks are marked with a $(\ast)$. In Figure 11, the coupling parameter is $\beta_{11} = -0.02$. 

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The essential point here is that comparison of the the \((E, \tau)\) plots for the uncoupled and resonantly coupled systems enables one to characterize, via changes in intensities of peaks associated with rational tori, the particular resonance coupling involved. In this sense the \((E, \tau)\) plots are a very informative pattern recognition tool.

**Single 1:2 resonance coupling term**

Single-resonance Hamiltonians with 2:1 stretch-bend (so-called Fermi resonance [10]) couplings

\[
H_{1:2}^{1:2} = 2\beta_{12} I_2 \sqrt{I_1} \cos(\psi_1 - 2\psi_2) \tag{35}
\]

have been widely used to fit CH stretch-bend spectra in HCX\(_3\) molecules [98]. Kellman and coworkers have shown that these systems can have a rich and complex phase space structure, where each vibrational polyad can be located in one of four “zones” representing a distinct kind of phase space morphology, and the system can pass from one zone to another by variation of parameters such as coupling strengths and polyad number [99].

Quantum \((E, \tau)\) plots have been computed for vibrational level spectra of Fermi resonant Hamiltonians for HCX\(_3\) [29]. Our po analysis of the Fermi resonant systems yields two main results. First of all, at the most qualitative level, the quantum \((E, \tau)\) plots immediately enable one to distinguish between spectra computed using two different Hamiltonians, one “diagonal” and the other “resonant”, which were used to fit a target spectrum, itself obtained using a slightly more complicated resonant Hamiltonian [100]. Moreover, the quantum \((E, \tau)\) plots for the resonant and target spectra are very similar, showing the clear superiority of the resonant fitting Hamiltonian to the diagonal version. Once again, the po analysis provides a generalized spectral pattern recognition tool, which analyzes local (in energy) oscillations in the level density.

Furthermore, a remarkable correspondence is found between the quantum \((E, \tau)\) plots and po structure on the polyad phase sphere (see Figure 12). In particular, we can recognize the characteristic signatures in the \((E, \tau)\) plots of the distinct zones defined by Xiao and Kellman [99], and are able to identify the bifurcations associated with transitions between zones. In this way we are able to follow a system as it passes (with increasing energy) from zone to zone.

The importance of recognizing and analyzing characteristic spectral patterns in strongly coupled systems has been stressed by Svitak et al., who examined level spacing patterns in Fermi resonant systems [100].

The Fermi resonant Hamiltonian discussed above exhibits a complicated phase space structure as a result of nearly resonant zeroth-order frequencies \((\Omega_{\text{stretch}} \simeq 2\Omega_{\text{bend}})\) and small anharmonicities. It is also of interest to discuss the addition of the coupling term \(H_{2:1}^{2:1}\) to the uncoupled Morse Hamiltonian \(H_0\) with \(\Omega_1 = 1.0, \Omega_2 = 0.8, \alpha_1 = -0.03, \text{ and } \alpha_2 = -0.02\). The quantum \((E, \tau)\) plot is shown in Fig. 13 for coupling strength \(\beta = -0.005\). The main point of interest is that the ridge associated with the 2:1 resonant torus has disappeared, signalling the breakup of the family of 2:1 resonant tori. The 1:1 and 2:2 ridges,
absent in Fig. 10, are present here, as the influence of the 2:1 resonant coupling does not affect the region of phase space occupied by the 1:1 rational tori.

**Two resonant coupling terms**

Now consider a Hamiltonian in which the coupling term \( H' \) is a sum of two resonant terms

\[
H' = H^{1:1} + H^{1:2},
\]

(36)

Such a multi-resonance Hamiltonian might be employed in fitting high-lying vibrational levels, for example [90].

The essential difference between the 2-resonance Hamiltonian and those discussed above is that the presence of a second coupling term destroys the invariance of the polyad number, so that the system is *nonintegrable*. The phase space structure then typically consists of a complicated interweaving of regular regions (tori, stable pos and surrounding islands) and irregular regions (unstable pos, cantori, homoclinic tangles): see Figure 14 [49]. Study of the classical-quantum correspondence for the 2-resonance Hamiltonian is currently in progress [92]. Of particular interest is the effect on the quantum \((E, \tau)\) plots for single resonance systems of the addition of a second coupling term. Can one, for example, follow the break-up of regular regions of phase space with increasing energy via intensity variations in peaks associated with rational tori?

Classical \((E, \tau)\) diagrams have been computed for a model 2-resonance spectroscopic Hamiltonian [92], where pos were calculated by iteration of symmetry lines [93]. The resulting plots have a very rich structure (Fig. 15). Of particular interest from the standpoint of classical mechanics is the ubiquity of pairs of orbits created by tangent bifurcations; such pairs of orbits emerge from the integrable limit by a route involving essentially 2-parameter bifurcations [94]. Thus, close to the integrable limit, an island chain bifurcation in the vicinity of a local mode po creates a stable/unstable pair of orbits associated with a given winding number. At higher energies a second island chain bifurcation creates a stable/unstable pair having a different winding number. Increasing the nonintegrability parameter then results in a pair of orbits having different winding numbers first merging and then splitting off to give a pair of orbits connected by tangent bifurcation (see Fig. 16). The two parameters in the present case are the energy \(E\) and the coupling parameter \(\beta_{12}\).

We are currently exploring this and related phenomena in the system of two coupled Morse oscillators [92]

### 3.5 Recent related work

We briefly mention some recent work related to the \((E, \tau)\) studies discussed here.

Pique and coworkers [83] have computed “vibrograms” \((E, \tau)\) plots using the experimental vibrational spectrum of CS\(_2\), and Joyeux has discussed the corresponding analysis for CO\(_2\) [84]. In both cases, analysis of the classical-quantum correspondence for 3D vibrational Hamiltonians was not complete. A
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vibrogram for NO$_2$ has also been computed [85]. Hirai and Heller have discussed the existence of a topological phase associated in connection with the vibrogram of a 2D model Hamiltonian exhibiting a homoclinic tangle [82]. Schinke and coworkers have computed vibrograms for PCN in an attempt to see quantum manifestations of tangent bifurcations [101].

Application of the $(E, \tau)$ method to realistic multimode systems faces a problem of resolution; that is, for a computation with a tractable basis size only a limited number of states falls within the energy window, so that peaks associated with pos of similar periods might not be well resolved. This problem can be overcome to a certain extent by reducing the effective value of $\bar{h}$ in theoretical computations [29]. Another possibility is to compute the density of states \( \rho \) as a function of \( z \equiv \bar{h}^{-1} \) at fixed classical energy \( E \) [102]; Fourier transformation then yields sharp peaks corresponding to classical actions \( \{S\} \) at energy \( E \). In an important advance, Main, Jung and Taylor have shown how to compute \( \rho(z,E) \) for Hamiltonians of the form

\[
\hat{H} = -\frac{1}{2z^2} \nabla^2 + V(x)
\]  

(37)

by transforming the usual Schrödinger equation to a generalized eigenvalue problem for eigenvalues \( \{z_j(E)\} \) [86]. It remains to extend the Main-Taylor method to spectroscopic Hamiltonians of the type discussed here, which are not homogeneous in \( z \). Use of spectral analysis methods more powerful than the discrete FFT should also help overcome the resolution problem [103].
4 Classical-quantum correspondence for multimode systems: beyond periodic orbits

4.1 General background

Real polyatomic molecules have at least 3 vibrational degrees of freedom. Both the classical and quantum mechanics of multimode systems pose considerable challenges to theory, and, despite enormous effort invested in “quantum chaology” in recent years [5, 6], the classical-quantum correspondence for such systems is relatively unexplored.

It is well known that classical $N \geq 3$ mode molecular vibrational Hamiltonians exhibit phenomena, such as crossing of resonance channels [40, 78, 104] and “Arnold diffusion” [105, 106, 107], that do not occur for 2 degrees of freedom. In particular, slow drift of action variables leads to long-time (classical) instability. In the mechanism proposed by Arnold [105], long-time drift occurs via the transverse intersection of stable and unstable manifolds of a chain of lower dimensional invariant tori created by the destruction of unperturbed $N$-tori along a given resonance. Such “Arnold diffusion” is mainly along resonance zones. As pointed out by several authors [107], this not the only possible mechanism for diffusion in phase space transport; in multimode systems, diffusion across resonance channels can be much more rapid than diffusion along resonance. The issue of what kinds of classical phase space transport do or do not constitute “Arnold diffusion” is in fact not yet settled [107]. In the molecular context we are interested in the quantum manifestations of all types of classical phase space transport in spectra and eigenstates. The important point is that there are always slow classical transport processes in multimode systems; a key question then concerns the relative importance of such processes as compared to slow nonclassical processes (e.g., dynamical tunneling [108]). It is known for 2D or 1½D systems that quantum interference effects suppress classical diffusion in action, leading to localization of quantum states [6]. On the other hand, nonclassical processes generally referred to as “dynamical tunneling” [108] can lead to interaction between zeroth-order states well separated in phase space, so enhancing mixing beyond that occurring classically.

Our research on these problems has involved detailed study of particular systems that are representative of a class of realistic molecular vibrational Hamiltonians. The aim is to use information about the classical dynamics (a difficult enough problem itself for $N \geq 3$ modes) to help analyze computed quantum properties (e.g., to assign spectra and eigenstates). The main focus of our studies to date has been the 3-mode Baggot vibrational Hamiltonian mentioned above [36, 37].

4.2 Classical and quantum mechanics of the H$_2$O molecule

We have diagonalized the 3-mode 2:2:1 resonant Baggot vibrational spectroscopic Hamiltonian for H$_2$O [89] in a basis of zeroth-order number states $|n_1, n_2, n_b\rangle$, and have studied the resulting quantum eigenstates [36, 37]. Conservation of
the quantum number $P = (n_1 + n_2) + n_b/2$ means that, for given $P$, the Hamiltonian may be diagonalized exactly in a finite Hilbert space; for example, there are 45 states in the manifold with $P = 8$.

Our approach has as its starting point a Chirikov analysis of the resonance channels for the Baggot Hamiltonian [35]. Chirikov analysis partitions phase space into regions corresponding to qualitatively different trajectory behavior: trajectories inside the resonance zone are strongly affected by a given resonance coupling term, whereas trajectories outside the resonance zone are essentially unperturbed. The method is an approximate, perturbative approach to the phase space structure of multimode systems, in that the different resonances are analyzed independently.

Chirikov analysis thus partitions the zeroth-order action space into resonance channels associated with each coupling term in the Hamiltonian (see Fig. 17). Using the classical resonance structure as a guide, we are able to organize eigenstates into families that form readily recognizable sequences along the resonance channels.

For example, Figure 18 shows action space projections for a sequence of eigenstates of the Baggot Hamiltonian that are localized inside the 2:1 resonance channel (note that there are two symmetry related 2:1 resonance channels, corresponding to the two equivalent stretch-bend resonances in H$_2$O. Using the classical resonance “template” we have been able to provide dynamical assignments for most of the eigenstates of the $P = 8, 16$ manifolds [36, 37].

Moving beyond the perturbative approximation of Chirikov resonance analysis, we have also examined quantum phase space (Husimi) density functions in order to undertake a more rigorous investigation of eigenstate delocalization. Dynamical assignments of vibrational eigenstates in the $P = 8$ and $P = 16$ manifolds have been made based upon invariant classical phase space structures, including but not limited to periodic orbits [36, 37]. For example, Fig. 19 shows the Husimi distribution function for an eigenstate of a modified version of the Baggot Hamiltonian containing only a single 2:1 resonance coupling term. This eigenstate is localized in the vicinity of a whiskered 2-torus, which is an analogue in the 3-mode case of an unstable periodic orbit in the 2-mode case [109].

It is important to note that the Baggot Hamiltonian for H$_2$O effectively has only 2 degrees of freedom, due to the conservation of $P$. Addition of extra resonant coupling terms, such as a 3:2 stretch-bend resonant interaction, will break the conservation of $P$, leading to a genuinely 3-mode problem with Hamiltonian $H'$. Eigenstates of $H'$ must then be found by diagonalizing in a large basis formed by manifolds of states with different $P$.

By computing eigenstates of $H'$, and by examining (suitably projected) action space and quantum phase space distribution functions, it should be possible to address several fundamental questions in the classical-quantum correspondence for multimode systems. For example, by examining the eigenstates of $H'$ in a basis consisting of the eigenstates of the Baggot Hamiltonian $H_B$, one can determine whether mixing occurs by classical mechanisms (diffusion along or across resonances), or by nonclassical “dynamical tunneling” [108].

The phenomenon of dynamical tunneling in multimode systems is of par-
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ticular interest [110, 111]. In integrable systems, dynamical tunneling gives rise to small splittings (for example, local mode splittings [112]) of the form \( \Delta E \sim A \exp(-S/\bar{\hbar}) \) [113] and to the formation of superposition states. In the absence of symmetry-related degeneracies, such interaction occurs between accidentally degenerate states involved in an “avoided crossing”.

For nonintegrable and for multimode systems more complicated interactions are possible. For example, in the phenomenon of chaos-assisted tunneling [114], the splitting between pairs of states is altered by interactions with other delocalized states. In our study of state mixing in the \( P = 8 \) manifold for the Baggot Hamiltonian, such an effective 3-state interaction near the physical parameter value was found to lead to a lack of assignability of a pair of states [36].

For 2D systems, the delocalized states are typically “chaotic”; for multimode systems, however, the interloper states may be delocalized but essentially regular as a result of the action of a single resonance coupling term. Moreover, as already mentioned, there are classical transport mechanisms that connect distant regions of phase space on long timescales that can “compete” with tunneling. The lack of a simple form (or good theory) for tunneling splittings in such a situation means that it is not simple to disentangle the different mixing mechanisms. The Baggot Hamiltonian is a useful vehicle for study of dynamical tunneling aspects of state-mixing in 3-mode systems. It exhibits pairs of closely spaced local-mode states, together with pairs of closely space stretch-bend resonant eigenstates; the latter can interact with ‘delocalized’ 1:1 resonant (normal) mode states, to give enhanced splittings, and also with nominally “chaotic” or delocalized states in the vicinity of the resonance junction. In contrast to the standard integrable case of, e.g., local mode splitting [110, 112], there exists a multiplicity of “paths” in state space connecting a given pair of states. As a challenge for the future, it remains to develop semiclassical theories for such dynamical tunneling phenomena.
5 Conclusion

In this chapter we have reviewed our recent work on the application of semi-classical periodic orbit theory to model hamiltonians of interest in atomic and molecular spectroscopy. Much work remains to be done on the classical, semi-classical and quantum mechanics of $N \geq 3$ mode systems; we have made a start in our work on the Baggot Hamiltonian for $\text{H}_2\text{O}$.

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Figure 1: Density $\rho(\varepsilon)$ of doubly-excited autoionizing resonances of the collinear He model as a function of the scaled energy $\varepsilon$. The density $\rho(\varepsilon)$ was computed using the stabilization method.
Figure 2: Power spectrum of $\rho(\varepsilon)$, the density of doubly-excited states for the collinear He model. Peaks appear at actions associated with classical periodic orbits at the energy $E_0 = -1$. 

Figure 3: Comparison of the analytical (upper panel) and numerical (lower panel) power spectra of the density of states for the integrable limit $\gamma \rightarrow 0$ of the coupled quartic oscillator Hamiltonian, eq. (2.5). Analytical results were obtained using the Berry-Tabor version of the trace formula.
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Figure 4: Power spectrum of the density of states for the coupled quartic oscillator system, eq. (2.5), as a function of the coupling parameter $\gamma$. Superimposed on this plot are traces of the action or half-action (depending on symmetry) of various classical periodic orbits at $E = E_0 = 1$. Units of action are $\hbar$. 
Figure 5: Surfaces of section with $p_2 = 0, E = 1.0$ for the coupled quartic Hamiltonian, eq. (2.5), $\eta_1 = 1.2, \eta_2 = 0.8$, showing the symmetric isochronous pitchfork bifurcation. (a) The central periodic orbit ($q_1 = p_1 = 0$) is unstable, and is flanked by two unstable “diagonal” periodic orbits ($\gamma = 1.4$). (b) The diagonal periodic orbits have merged with the central orbit leaving an unstable central periodic orbit ($\gamma = 1.8$). The classical bifurcation occurs at $\gamma = 1.6$. 

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Figure 6: Power spectrum of the density of states for the coupled quartic oscillator system, eq. (2.5), for reduced action values close to that of the central periodic involved in the symmetric pitchfork bifurcation shown in Fig. 5, $S = 0.832$. A range of coupling parameters in the vicinity of the classical bifurcation point $\gamma = 1.6$ are shown. (a) Numerical results obtained by matrix diagonalization. (b) Analytical results obtained by uniform semiclassical analysis.
Figure 7: Comparison of classical and quantum $(E,\tau)$ plots for a 1D Morse oscillator. Parameter values: $\Omega = 1, \alpha = -0.03, \hbar = 1/80$ (a) Classical. (b) Quantum. (Positions of peaks in the quantum $(E,\tau)$ plot are shown.)
Figure 8: Classical \((E, \tau)\) plot for uncoupled Morse oscillators. Parameters values: \(\Omega_1 = 1.0, \Omega_2 = 0.8, \alpha_1 = 0.03, \alpha_2 = 0.02\).
Figure 9: Quantum $(E, \tau)$ plot for uncoupled Morse oscillators. Parameters values: $\Omega_1 = 1.0, \Omega_2 = 0.8, \alpha_1 = 0.03, \alpha_2 = 0.02$. (cf. Figure 8)
Figure 10: Quantum \((E, \tau)\) plot for coupled 1:1 local modes. Parameter values: 
\(\beta = 0.01, \Omega_1 = \Omega_2 = 0.5, \alpha_1 = \alpha_2 = -0.001.\)
Figure 11: Quantum $(E, \tau)$ plot for 2 Morse oscillators coupled by a single 1:1 coupling term. Parameter values: $\Omega_1 = \Omega_2 = 0.5$, $\alpha_1 = \alpha_2 = -0.001$, $\beta = -0.02$. (cf. Figure 9)
Figure 12: Comparison of classical and quantum $(E, \tau)$ plots for a model Hamiltonian describing CH stretch-bend interaction in HCX$_3$ molecules. (a) Classical periodic orbit periods versus energy. (b) Corresponding quantum $(E, \tau)$ plot.
Figure 13: Quantum $(E, \tau)$ plot for 2 Morse oscillators coupled by a single 2:1 coupling term. Parameter values: $\Omega_1 = \Omega_2 = 0.5$, $\alpha_1 = \alpha_2 = -0.001$, $\beta = -0.005$. (cf. Figure 9)
Figure 14: Classical surface of section \((p_2 = 0)\) for Morse oscillator Hamiltonian with two resonance coupling terms. Parameter values: \(E = 4.8, \Omega_1 = 1.0, \Omega_2 = 0.8, \alpha_1 = 0.03, \alpha_2 = 0.02, \beta_{11} = 0.01, \beta_{12} = 0.02\). One symmetry line is the axis \(p_1 = 0\); a second symmetry line is shown as a thick line.
Figure 15: Classical $(E, \tau)$ plot for Morse oscillator Hamiltonian with two resonance coupling terms. Parameter values: $\Omega_1 = 1.0$, $\Omega_2 = 0.8$, $\alpha_1 = 0.03$, $\alpha_2 = 0.02$, $\beta_{11} = 0.01$, $\beta_{12} = 0.01$. 

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Figure 16: Orbit bifurcation sequence in coupled Morse oscillator system as seen in classical $(E, \tau)$ plot. Parameter values: $\Omega_1 = 1.0$, $\Omega_2 = 0.8$, $\alpha_1 = 0.03$, $\alpha_2 = 0.02$, $\beta_{11} = 0.01$. (a) Prior to bifurcation, $\beta_{12} = 0.018$, 4 period-four periodic orbits (small circles) emerge from the central local mode orbit (large circles). (b) After bifurcation, $(\beta_{12} = 0.023)$, the 4 period-four orbits have merged in pairs to give 2 pairs of orbits apparently created via tangent bifurcations (small circles).
Figure 17: Classical resonance channel structure for the Baggot Hamiltonian for H₂O. The polyad quantum number $P = I_1 + I_2 + I_b/2 = 16$. Primary periodic orbits (●) and resonant 2-tori (×) are shown.
Figure 18: Action space projections of a sequence of eigenstates of the Baggot Hamiltonian localized in the 2:1 resonance channels. Eigenstates are represented by plotting at every physical lattice point a circle with radius equal to the square of the coefficient of the corresponding zeroth-order basis state in the eigenstate of interest. To distinguish the eigenstates in the sequence we plot them with different line thicknesses.
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Figure 19: Husimi phase space distribution for a resonant eigenstate localized in the 2:1 resonance channel in the vicinity of a whiskered 2-torus, the multidimensional generalization of an unstable periodic orbit.