ANALYSIS OF QUANTUM EIGENSTATES IN A 3-MODE SYSTEM

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Abstract. We study the quantum eigenstates of a three degree of freedom spectroscopic Hamiltonian for the H_2O molecule. Using the classical resonance zones as a *template*, we are able to understand and organize the energy level spectrum, and provide quantum number assignments for the eigenstates.

1. Introduction

The problem of the nature of highly excited rovibrational states of polyatomic molecules is of central significance for molecular spectroscopy and chemical kinetics [1]. At high energies, the traditional approach of molecular spectroscopy, based on on a harmonic oscillator-rigid rotor model [2], breaks down due to strong intermode couplings. These mode couplings, which result from anharmonicities in the potential and/or rotation-vibration interaction, lead to intramolecular vibrational energy transfer [3] and complicated energy spectra.

A typical classical polyatomic molecule Hamiltonian is inherently a multi ($N \geq 3$) mode, nonintegrable system. Moreover, at high levels of internal excitation, the semiclassical regime is approached, and the general problem of the classical-quantum correspondence for nonintegrable systems must be faced in order to relate classical and quantum aspects [4].

For both $N = 2$- and $N \geq 3$-mode systems, we can recognize several mechanisms leading to complicated energy level patterns. One possibility involves strong mixing of near-degenerate manifolds of states by a single resonant coupling, so that the corresponding classical dynamics is still integrable. Another possibility is strong state mixing due to the presence of two or more resonant couplings, so that the corresponding classical dynamics is nonintegrable and we have the possibility of chaos. Finally, there is the possibility of state mixing due to the phenomenon of "dynamical tunneling" [5], associated with accidental near-degeneracies of levels.

Model spectroscopic Hamiltonians describing two modes coupled by a single resonant term have been widely studied [6]. For such systems there exists an additional constant of motion apart from the energy, and the reduced phase space is a 2-dimensional sphere, the so-called *polyad phase sphere*. Kellman and coworkers have studied the bifurcation structure of fixed points of the reduced Hamiltonian on the polyad phase sphere, which correspond to the periodic orbits in the full phase space, and have investigated in detail the

relation between the classical phase space structure and the associated quantum mechanics [6]. For the case of a single resonant coupling, Rose and Kellman have extended this analysis to a multimode planar model of C_2H_2 [7].

Multimode Hamiltonians with two or more resonant couplings have not been studied in a systematic fashion. One reason is that, for multidimensional systems, the stable and unstable manifolds of unstable periodic orbits cannot partition phase space into disjoint "zones" [8], thereby preventing straightforward generalization of periodic orbit based approaches.

The classical mechanics of multimode systems is of course considerably richer than that of 2-mode Hamiltonians: there is the possibility of Arnold diffusion [9], and, of more immediate relevance to molecular problems, the existence of *intersections* between resonance zones. The implications of this latter feature of the phase space structure of multi-mode systems have begun to be explored for molecular systems [10].

In the present paper we outline a qualitative approach to analysis of energy level patterns and wavefunctions in multimode systems, which is based on Chirikov resonance analysis [9]. The system studied is a 3-mode spectroscopic vibrational Hamiltonian for H_2O due to Baggot [11]. We establish a direct correlation between features of the associated eigenstates with the location of resonance zones in phase space. In particular, we observe progressions of resonant eigenstates *along* classical resonance zones leading to "mixed" states in the vicinity of the resonance channel intersections. The classical resonance analysis therefore provides a *template* for analyzing the quantum states, and thereby facilitates an understanding of the level spectrum.

2. Resonance analysis of the Baggot Hamiltonian

We consider the classical analog of the spectroscopic Hamiltonian for H_2O derived by Baggot [11]. This 3 degree of freedom Hamiltonian describes the two local OH stretching modes and the HOH bend, and includes two 2:1 stretch-bend resonant terms $\mathcal{H}_r^{2:1}, r = 1, 2$, a 1:1 stretch-stretch resonant term $\mathcal{H}^{1:1}$ and a 2:2 stretch-stretch resonant term $\mathcal{H}^{2:2}$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}^{1:1} + \mathcal{H}^{2:2} + \sum_{r=1,2} \mathcal{H}_r^{2:1}, \tag{1}$$

where $\mathcal{H}_0$ is the zeroth order Hamiltonian

$$\mathcal{H}_0 = \Omega_s \sum_{r=1,2} I_r + \Omega_b I_b + \alpha_s \sum_{r=1,2} I_r^2 + \alpha_b I_b^2 + \epsilon_{ss} I_1 I_2 + \epsilon_{sb} I_b \sum_{r=1,2} I_r, \tag{2}$$

and the resonant coupling terms are

$$\begin{aligned} \mathcal{H}^{1:1} &= \beta_{12}'(I_1 I_2)^{1/2}\cos(\theta_1 - \theta_2) \\ \mathcal{H}^{2:2} &= \beta_{22} I_1 I_2 \cos[2(\theta_1 - \theta_2)] \\ \mathcal{H}_r^{2:1} &= \beta_{sb}(I_r I_b^2)^{1/2}\cos(\theta_r - 2\theta_b). \end{aligned} \tag{3}$$

In the above equations, $(\mathbf{I}, \boldsymbol{\theta})$ are the canonical action-angle variables for the two stretches and the bend mode, respectively, with $\beta_{12}' \equiv \beta_{12} + \lambda'(I_1 + I_2) + \lambda'' I_b$. Values of the various parameters are taken from Baggot's fit to the vibrational levels of H_2O (Table 2 of reference [11]). The 2:2 resonance coupling does not significantly affect the classical

phase space structures in the regime of interest for this paper and will be neglected in the classical resonance analysis.

The complete Hamiltonian $\mathcal{H}$, although nonintegrable, has a constant of the motion in addition to the energy:

$$\mathcal{N} = 2 \sum_{r=1,2} I_r + I_b, \tag{4}$$

which is the classical analog of (twice) the *polyad number*, $\mathsf{P} = \sum_{r=1,2} n_s + n_b/2$. Thus the dynamics is constrained to the plane in action space $\mathcal{N} = \text{constant}$. Chirikov resonance analysis for $\mathcal{H}_0$ is straightforward, and in standard fashion one can determine the location of the resonance zones in action space [9]. Both the 1:1 and 2:1 resonance zones are shown in Figure 1, projected onto the (I_1, I_2) action plane ($\mathsf{P} = 8$). It is important to note that, for the Baggot Hamiltonian, as $\beta_{12} < 0$ and $\lambda' > 0$ the 1:1 resonance width actually *decreases* as the actions I_1, I_2 get larger. Note also that we do not explicitly consider secondary resonances since we are interested only in the large-scale structure of the classical phase space (i.e., intersection of the lowest order resonance zones).

3. Analysis and assignment of eigenstates and spectra

The quantum eigenfunctions and eigenenergies were obtained by diagonalizing the Baggot Hamiltonian in the number basis $|n_1, n_2, n_b\rangle$, where n_1, n_2 are the quantum numbers for the anharmonic local O-H stretch modes and n_b denotes the bend quantum number. The Hamiltonian is block diagonal in the polyad number P, and the total number of states at fixed P is $(\mathsf{P} + 1)(\mathsf{P} + 2)/2$. To analyse the eigenstates, it is natural to project them onto the (n_1, n_2) quantum number (action) plane. The physical points in the (n_1, n_2) lattice are those points for which $\mathsf{P} - n_1 - n_2$ is nonnegative. The 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.

In this paper we concentrate on the $\mathsf{P} = 8$ case. There are a total of 45 states and for this case the 1:1 and 2:1 resonance lines do not intersect in the physical action space. Moreover, the 1:1 resonance interaction dominates in the sense that an appropriate zeroth-order picture of the spectrum is one in which only the 1:1 coupling is present, i.e., the bend quantum number n_b is conserved. In this (classically integrable) limit we have essentially a stack of independent 2-mode systems, labelled with the quantum number n_b. States for the 1:1 coupled local modes are classified as "local" or "normal", according to whether amplitude is situated outside or inside the 1:1 resonance zone, respectively. In the absence of 2:1 couplings, each eigenstate has nonzero amplitude only along the line $I_1 + I_2 = \text{constant}$. The normal mode states form progressions *along* the 1:1 resonance line, where all states in a given sequence have either a node or antinode along the diagonal. Figure 1a shows one particular sequence in the case when only the 1:1 interaction term is present.

Of key interest is the effect of the 2:1 resonant couplings on this zeroth-order picture; the 2:1 couplings couple together stacks of states with different values of n_b, thereby manifesting the true multidimensional nature of the system. Figure 1b shows a sequence of states for the fully coupled system corresponding to those of Fig 1. It is clear that, in the nonintegrable case, one of the states in the sequence is significantly distorted by the 2:1 resonant term (this state is marked with thick circles). For larger values of the polyad number P, we observe progressions of resonant states along the 2:1 resonance channels.
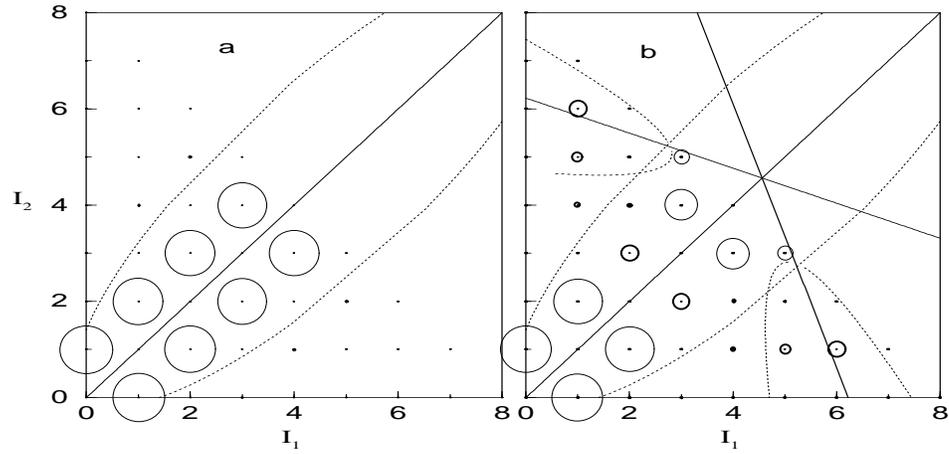
Figure 1. Normal mode sequence along the 1:1 resonant line for the integrable case (a) and nonintegrable case (b).
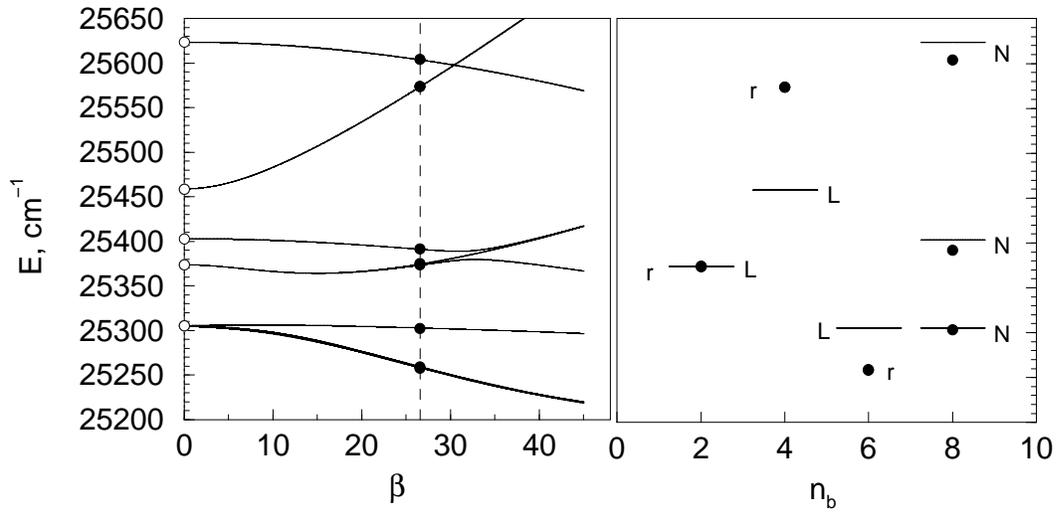

Figure 2. (a) Evolution of the energy spectrum as $\beta \equiv \beta_{sb}$ is turned on and (b) associated states grouped by n_b. N, L and r stand for normal mode, nonresonant local mode doublets and resonant local mode doublets respectively.
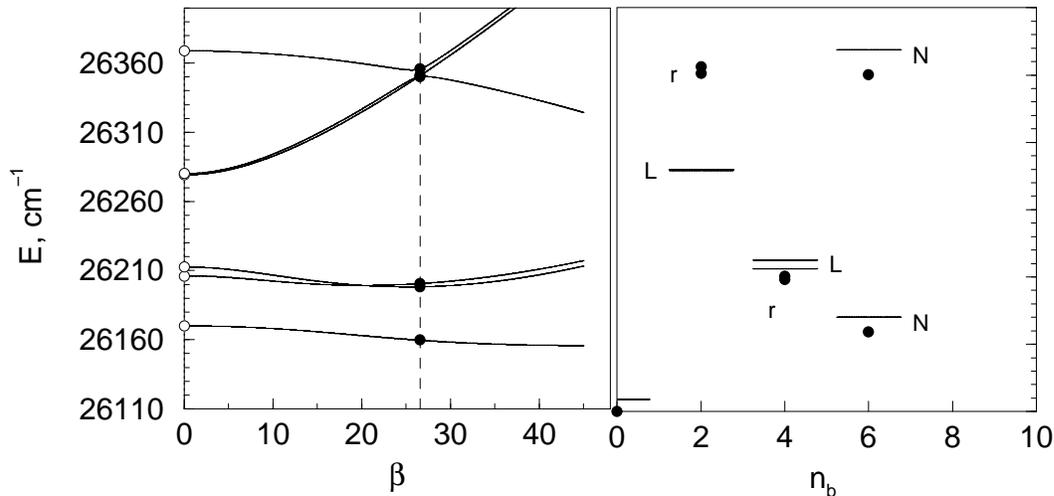
Figure 3.   Same as figure 2 with a different region of the energy spectrum.

We now examine the changes in the level spectrum for the 1:1 coupling case when the 2:1 couplings are turned on. Figures 2 and 3 show the parts of the spectrum which undergo the most significant changes for $P = 8$. Local mode ($\pm$) doublets situated in the vicinity of the phase space region corresponding to the 2:1 resonance zone become *2:1 resonant doublets* under the influence of the 2:1 couplings. Most of the mixing occurs between the $n_b = 2, 4$ and 6 manifolds of states, which correlates well with location of the 2:1 resonance zone. All of the avoided crossings seen in Figures 2 and 3 are simple two state crossings. For $P = 8$, one can therefore understand the mixing of states from different n_b manifolds via simple two state analysis. The assignment of the spectrum is straightforward, due to the approximate conservation of n_b, and states are assigned as normal mode, nonresonant local mode doublets, or 2:1 resonant local mode doublets.

The simple two state scenario breaks down at higher values of P where one sees complicated mixings involving three or more states. In such cases it becomes more useful to organize the spectrum on the basis of the quantum numbers associated with resonant sequences as opposed to the n_b grouping. The details of the analysis for higher values of P will be reported in a future publication [12].

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