

## Phase space, Topology, and Molecules.

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In spectroscopy we choose a set of quantum numbers for assigning a spectrum. However, there are cases when a set of quantum numbers cannot be used globally. This happens when excitation of a molecule results in a *qualitative* change of the energy level pattern. Recent examples are “quasilinear” molecules - *i.e.* molecules exhibiting Quantum Monodromy. In such molecules bent-molecule vibration-rotation quantum numbers are most appropriate for lower rovibrational levels while linear-molecule quantum numbers can be more appropriate for higher levels.

The question we are examining is to what extent fundamental notions from geometric mechanics and topology allow us to localize the energies and angular momenta where such rearrangement occurs. This talk begins with a reminder that phase space is simply configuration space supplemented by the momentum coordinates. Fig. 1 shows the 1 dimensional (1D) configuration space example of a Simple Harmonic Oscillator.

Supplementing this with the single momentum coordinate results in a 2D phase space. Fig. 1 also shows a phase space trajectory for a SHO with a specific energy.

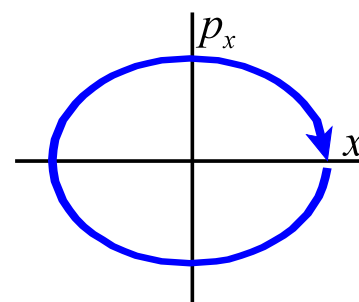


Figure 1. Phase space diagram for Simple Harmonic Oscillator

If motion occurs in 2D then supplementing the two configuration space dimensions by the two momentum dimensions results in a 4D phase space. This is difficult to illustrate! However, in the problems of interest angular momentum is conserved. Choosing angular momentum as one of the two momenta of the system leaves us with a set of 3D problems, one for each value of the angular momentum. These are much easier to illustrate and understand than 4D ones! The set of phase space trajectories for a given energy and angular momentum typically form a torus (doughnut). Fig. 2 shows an example for gravitational orbital motion. Elliptical orbits for the same energy and angular momentum but with different starting points are shown, along with their phase space trajectories. It can be seen that the full set of these phase space trajectories combine to cover a torus, which is also shown.

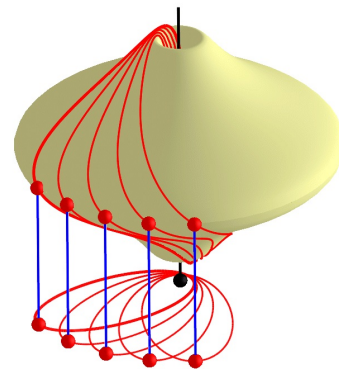


Figure 2.  
Bottom: Elliptical gravitational orbits around the black point - all with the same energy and angular momentum but different starting points.  
Top: Corresponding phase space trajectories and the resulting torus.

More interesting is the case of the double-minimum EF electronic state of molecular Hydrogen. For vibrationally bound energies for  $J=10$  three different regimes can be seen in Fig. 3. For the energy shown in panel (a) only the outer-well is classically accessible. In (b) both wells are separately accessible, while in (c) the wells are jointly accessible. The resulting phase-space tori are also shown in each panel. For energies similar to that shown in (a) there is a single torus,

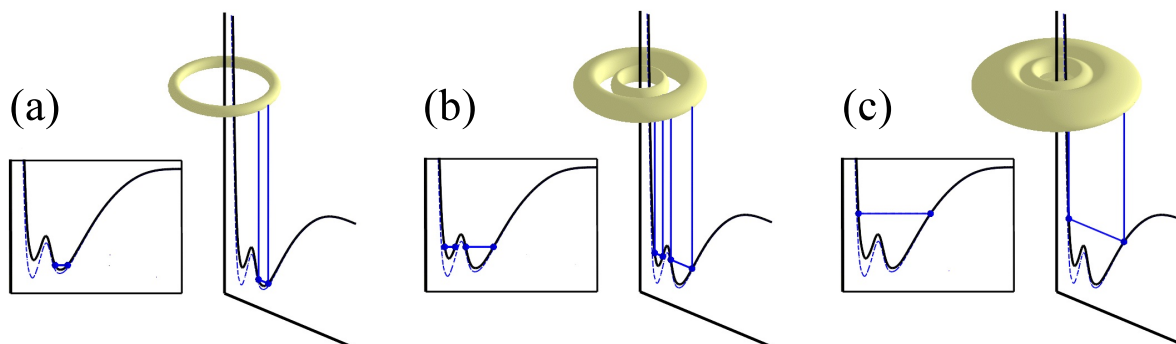


Figure 3. Effective potential energy function for  $J = 10$  for the EF state of  $H_2$ , along with classically allowed ranges. Phase space surfaces (topologically these are tori) are shown for each selected energy. Vertical lines connect classical turning points with edges of tori.

corresponding to vibration in the outer well along with rotation of the molecule. For (b) there is a torus for each well, while in (c) these two tori have joined, forming a single “dented” torus.

The boundaries between regions of different behaviour are curves in Energy-Momentum space. These curves are called *Critical Curves* and topological considerations allow us to find the Critical Curves with remarkable ease. The critical curves for the EF state of Hydrogen are shown as functions of angular momentum in Fig. 4.

Also shown in Fig. 4 are the quantum energy levels of this state (for clearer representation the diagram is mirrored around  $J=0$ ).

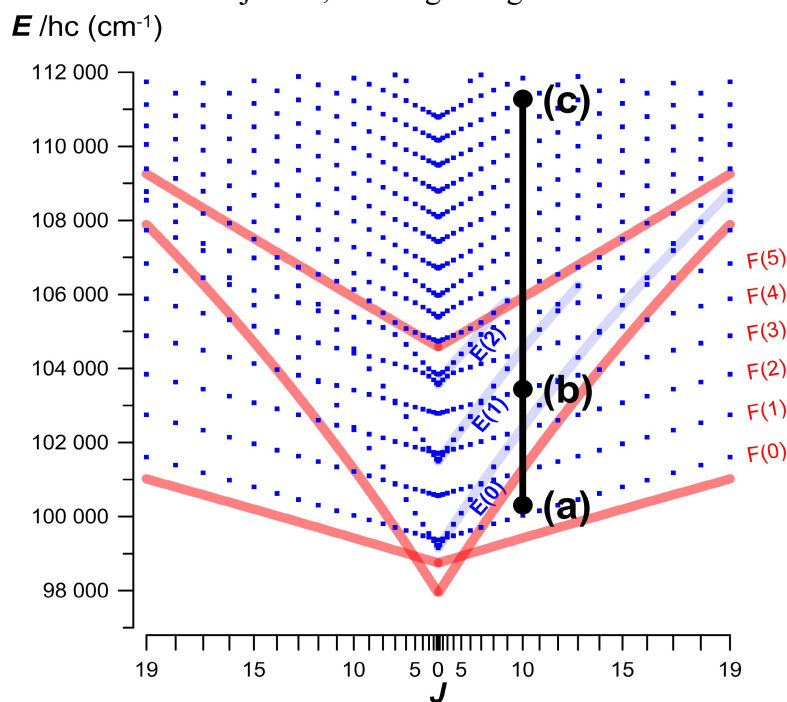


Figure 4  
EF State quantum levels of  $H_2$  shown with the Critical Curves. Dots indicate  $J = 10$  levels of Fig. 3. (Levels calculated by MQDT and agree to within  $\sim 5 \text{ cm}^{-1}$  of experiment, where the latter is known.)

The rearrangement of the energy level grid whenever one of the Critical Curves is crossed is clearly evident in Fig. 4. Such dramatic rearrangement of the quantum levels generally requires the use of different quantum numbers in each region. If one is using an effective model to describe the quantum levels then different models will have to be used in each region.

This type of dramatic rearrangement occurs in other molecular systems, including the already mentioned example of vibration-rotation in Quantum Monodromy and torsion-vibration in skew-chain molecules. Time permitting, these examples will also be presented.

Reference: *Topological Insight into the Patterns of Quantum Energy Levels of the EF State of Molecular Hydrogen*, Francis Bischoff, UNB Physics Honour's B.Sc. Thesis, 2013.