On the Significance of Classically Periodic Orbits in the Interpretation of Vibrational Energy Eigenstates

T. Weston, Worcester College

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Molecular vibrational eigenstates are considered in terms of periodic orbit quantization schemes. Quantization formulae, derived from summation over the repetitions of primitive periodic orbits prove satisfactory to describe low energy normal mode vibrations, and using the properties of the periodic orbits of nonlinear dynamical systems the phenomenon of vibrational resonance is related to periodic orbit bifurcations.

In order to extend this semiclassical description to spectroscopic intensity data, a periodic orbit description of Franck-Condon factors is derived. Consideration of this formula indicates a spectral signature of certain periodic orbit bifurcations.

With a view to obtaining qualitative information on vibrational eigenstates methods of obtaining periodic orbits in vibrational systems are critically discussed. A method of mapping potential contours and symmetry lines is reconsidered and shown to find structurally stable periodic orbits and also provides a generic description of saddle-node bifurcation cascades in highly excited molecular systems.

The method of Hill is used as a method to describe periodic orbit stability and infer bifurcation structure. A novel asymptotic method is described to solve the driven oscillator equations involved. Application of this method to the coupled Morse oscillator model of triatomic stretching vibrations yields an analytic solution which reveals a rich structure of resonant behaviour and provides a unified description of such vibrations within the model.

Quantal and classical numerical calculations are presented for this model which confirm the Hill's analysis and reveal the predicted saddle-node dynamics. Quantum eigenstates are analysed using the semiclassical quantization formulae and numerically using coherent state phase space representations and Franck-Condon spectra and many periodic assignments are given. A route to global chaos is also revealed, the mechanism of which is seen to be the accumulation of high order bifurcations about the symmetric stretch, predicted by the Hill's analysis.

Finally, as an initial exploration of these effects in higher degrees of freedom the in-plane bending motion is included along with the stretching modes in the analysis of the symmetric stretch orbit stability and a pronounced periodic-doubling bifurcation is observed and related to the Fermi resonance in such systems.