QUANTUM LEVEL STRUCTURES AND NON-LINEAR CLASSICAL DYNAMICS

M. S. CHILD, *Physical and Theoretical Chemistry Laboratory, South Parks, Rd, Oxford OX1 3QZ, United Kingdom.*

It is well known that certain wavefunctions follow the shapes of classical trajectories close to stable classical periodic orbits. This paper concerns a deeper relationship between the organization of quantum mechanical eigenvalues and the number and types of classical periodic orbits, illustrated by reference to effective spectroscopic Hamiltonians[a]. The simplest cases are perhaps the local stretching states of H_2O or H_2S, for which one sees a pattern of progressively close local mode doublets at energies below the separatrix associated with an unstable orbit, and an increasingly regular pattern of energy separations above it. Similar, but more complex behavior is found in highly excited Fermi resonance polyads. There is also a classically related generic pattern (termed quantum monodromy[b]) in the level structures arising from any cylindrically symmetric saddle point. Examples will be given for the bent to linear states of H_2O, pendular states of dipolar molecules in electric fields and highly excited Fermi resonant states of CO_2.

[a] M S Child in '*Computational Molecular Spectroscopy*', Eds P Jensen and P R Bunker (Wiley, 2000)

[b] M S Child, T Weston and J Tennyson, Mol Phys, **96**, 371 (1999)