ROVIBRONIC PHASE PLOTS I: COMPUTER GRAPHICAL INSIGHTS INTO TENSOR SYMMETRY BREAKING, DYNAMICS AND SPIN-SYMMETRY-SPECIES CONVERSION EFFECTS

JUSTIN C. MITCHELL and WILLIAM G. HARTER, *Department of Physics, University of Arkansas, Fayetteville, AR 72701*.

At the core of molecular spectral assignment (and quantum theory in general) is a process of matrix diagonalization for eigensolutions. An n-by-n matrix goes in and n eigenvalues with $n(n-1)$ eigenvector components come out. Yet one may be left mystified by both the numerical processes and the physical processes that the numbers supposedly represent.

The n-values (or differences thereof) give spectra, but the bulk of the information about dynamics, intensity, symmetry, etc. lies in the $n^2 - n$ vector components. This and the following talk shows ways to understand and approximate results of rovibrational diagonalizations that insightfully display and relate e-values together with e-vectors.

Centrifugal and Coriolis effects on rovibrational eigensolutions are often amenable to approximation by rotational-energy-surfaces (RES) that serve both as an angular phase space and as an Euler body-coordinate space. An illustration of RES views of SF_6 fine and superfine spectral structure[a] is reviewed and compared to extensions of this technique to higher rank tensor models.[b]

Of particular interest are spectral and RES regions with "big-pocket" suffering spontaneous symmetry breaking or phase localization effects including breakdown of Herzberg spin-species-conservation rules [c] [d] and superhyperfine clustering.[e] The RES views help expose the wave interference phenomena that deeply underlie rovibronic dynamics as well as clarifying the matrix diagonalization methods that quantify them.

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[a] W. G. Harter, in Handbook of Atomic, Molecular and Optical Physics, edited by G.W.F. Drake (Springer, Germany 2006) Chapter 32. p. 501.
[b] W. G. Harter, J. Math. Phys. 20, 1453 (1979).
[c] G. Herzberg, Infrared and Raman Spectra (VanNostrand 1945) pp. 458,463.
[d] J. T. Hougen, T. Oka, Science, 310, 1913 (2005)
[e] W. G. Harter, Phys. Rev. A24,192-262(1981)