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

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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 n² − 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 SF₆ fine and superfine spectral structure is reviewed and compared to extensions of this technique to higher rank tensor models.

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 and superhyperfine clustering. 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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