ROVIBRONIC PHASE PLOTS II: MULTI-SURFACE ROTATIONAL ENEGRY ANISOTROPY FOR INTERNAL-ROTOR MOLECULES AND ROTATIONAL JAHN-TELLER-RENNER ANALOGS

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

Born-Opppenheimer-Approximations (BOA) suppose potential-energy-surfaces (PES) represent adiabatic variation of an electronic eigenstate energy due to slower nuclear vibrational motion. By analogy, rotational-energy-surfaces (RES) of talk (I) suppose adiabatic variation of vibrational eigenstate energy due to slower rotational motion, and, as such, represent a slow-motion BOA.
Jahn-Teller-Renner (JTR) breakdown of simple BOA occurs if an electronic degeneracy allows resonance between vibrational modes and two or more electronic eigenstates that involve two or more PES that engage in varying degrees of avoid-crossing-dynmaics (ACD). By analogy, two or more RES must engage in rotational ACD if multiple vibrational modes become resonant with overall rotation.[a] [b]
An example of RES-pair is illustrated by models of a molecule with a single rotating "pinwheel" under a variety of conditions and constraints. The simplest case is a classical spherical rigid rotor with a single fixed classical spinning "gyro" rotor attached.
The next most complicated cases are symmetric or asymmetric rotors with the gyro fixed in symmetric or asymmetric attitudes. Then the gyro as a quantum spin illustrates RES-ACD and finally fully quantum-spin-rotor eigensolutions may be compared to the classical and semi-classical approximations.

[a] W.G. Harter, Comp. Phys. Reports 8, 6 (1988) p373-384
[b] Ortigoso, Kleiner, Hougen J. Chem. Phys. 110, 11688 (1999)