MULTI-VALUED VERSUS SINGLE-VALUED LARGE-AMPLITUDE BENDING-TORSIONAL-ROTATIONAL COORDINATE SYSTEMS FOR SIMULTANEOUSLY TREATING TRANS-BENT AND CIS-BENT ACETYLENE IN ITS S_1 EXCITED ELECTRONIC STATE

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There are now a large number of papers in the spectroscopic literature which make use of multiple-valued (frequently double-valued) coordinate systems and multiple-groups of the permutation-inversion group to deal with the symmetry properties of large-amplitude motions in molecules of high symmetry. The use of multiple-valued coordinate systems, and the resultant appearance of more minima on the potential surface than would be found on the surface for a single-valued coordinate system, can lead to conceptual discomfort and questions of mathematical legitimacy. In the present talk we show that treatments using multiple-valued coordinate systems simply represent one scheme for applying the appropriate quantum mechanical boundary conditions to Schrödinger's equation defined in a single-valued coordinate system. The demonstration is not general, but rather focusses on the specific example of a non-linear electronic state of C_2H_2 and on the two-fold and eight-fold extended permutation-inversion groups recently introduced to treat simultaneously symmetry questions in trans-bent and cis-bent acetylene. Some discussion of the mathematical convenience lost by insisting on using a single-valued coordinate system will also be presented.