Jahn-Teller theory beyond the standard model

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The standard model of Jahn-Teller (JT) theory is defined by the reviews and monographs on the JT effect [1]. It is based on the Taylor expansion of the electrostatic (spin-free) electronic Hamiltonian up to second order in normal-mode displacements at the reference geometry and the approximation of the spin-orbit (SO) coupling operator in zeroth order of the normal-mode expansion. For the construction of accurate ab initio potential-energy surfaces for large-amplitude motion in JT systems, these approximations are not sufficient. In this talk, the expansion of the electrostatic Hamiltonian up to high orders in symmetry adapted polynomials is discussed for trigonal [2] and tetrahedral [3, 4] systems. Multidimensional JT and/or pseudo-JT potential-energy surfaces are constructed making use of large sets of ab initio data at the CASSCF or CASSCF/MRCI levels. The SO coupling is treated up to first order in normal-mode displacements, starting from the microscopic Breit-Pauli SO operator, thus accounting for linear JT couplings which are of relativistic origin [5, 6]. The relevance of higher-order electrostatic as well as linear relativistic JT coupling terms is illustrated by the calculation of vibronic spectra for molecular systems containing transition metals or heavy main-group elements.

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