Vibronic and Spin-Orbit Vibronic Hamiltonian Formalism for Axial Symmetries

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Jahn-Teller (JT) and pseudo-Jahn-Teller (pJT) interactions find far-reaching consequences in spectroscopy, structural chemistry, solid state physics, and materials science. They belong to a broader concept of vibronic interaction, with their origins closely related to symmetry. For systems containing heavy atoms, JT and pJT interactions shall be considered on an equal footing with spin-orbit interaction. The accuracy of simulating those interactions critically depends on the quality of the relevant vibronic and spin-orbit vibronic Hamiltonians. In general, the accuracy is enhanced when the Hamiltonian matrix elements are expanded as higher order polynomials of vibrational coordinates. However, the general expansion formulas of those matrix elements were unknown. In the past few years, we endeavoured to derive general expansion formalism for vibronic and spin-orbit vibronic Hamiltonians.[1-7] In this presentation, I will present the specific Hamiltonian formalism for systems in axial symmetries (i.e., from C_1 to $D_{\infty h}$), and its application [4] in studying photo-detachment spectrum of CO_3^-. I will also present a program, VHEGEN (Vibronic Hamiltonian Expansion GENerator), which generates expansion formulas for all axial JT and pJT Hamiltonians.[6]

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