

Density Functional Theory and Intrinsic Distortion Path in the analysis of the Jahn-Teller effect

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Despite the great progress and development of various experimental techniques for studying the Jahn-Teller (JT) effect, computational methods are necessary to understand the microscopic origin and to get deeper insight into the vibronic coupling effects.

A method for the calculation of Jahn-Teller parameters, within the DFT framework, has been developed and applied with a good accuracy for the analysis of JT-active molecules. In order to tackle the multimode problem, the Intrinsic Distortion Path (IDP) analysis has been proposed, in which the distortion is represented as a superposition of all totally symmetric normal modes in the Low Symmetry (LS) minimum energy conformation. Although the specific formulation of the JT distortion in terms of the Hessian of the LS minimum has several advantages, this is in contrast with the usual treatment of the Jahn-Teller effect, starting from the High Symmetry (HS) point of the Adiabatical Potential Energy Surface. However, all the required information to calculate the vibronic coupling coefficients is also contained in the LS structure. Within the harmonic approximation the potential energy surface has a simple analytical form. This allows to directly obtain the forces at the HS point, without any fitting, and thus avoids the problems of calculating energies and gradients around the HS cusp.

In order to illustrate the method, an analysis of the JT distortion in the cyclopentadienyl radical, fullerene ions, tris(ethylenediamine)copper(II) and bis(1,4,7-triazacyclononane) complexes of some first-row transition metal cations will be presented.

This conceptually simple model gives direct insight into one of the essential problems in physical chemistry: the coupling between the electron distribution and the motion of the nuclei.