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Modeling Cusps in Adiabatic Potential Energy Surfaces Using a Generalized Janh-Teller Coordinate

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Abstract

A recent generalization of the Jahn-Teller coordinate proposed for modeling cusps on single-sheeted adiabatic potential energy surfaces for triatomics is extended to any type of crossing seam. The model is applied to the $^2A''$ state of NO_2 and the more complicated $HN_2(^2A')$ system, which shows permutationally equivalent and strongly curved seams.

1. Introduction

The presence of conical intersections causes cusps in the adiabatic energies of both ground and excited electronic states, which in turn makes the use of smooth functions unsuitable for modeling such regions of the molecular potential energy surface (PES). The problem may be solved by first performing an adiabatic-to-diabatic (ATD) transformation on the *ab initio* energies followed by modeling the smooth diabatic states so obtained. Such diabatic states can then be back transformed to the adiabatic representation with the proper cusp behavior. Unfortunately, the ATD transformation process is not unique which has led to the design of distinct approaches for specific purposes.[1,2,3,4,5,6,7,8,9,10,11] Moreover, when applied to the description of crossing seams in PESs such approaches must often be used in conjunction with the PES modeling scheme, thence making the overall process of obtaining a multisheeted global PES rather cumbersome.

Recently, following pioneering work by Murrell and one of us,[12] we have explored an alternative approach to adiabatic PES that allows the proper description of crossing seams in triatomic systems without the need of employing any ATD transformation.[13] In fact, a detailed application of the method for constructing an accurate PES for the adiabatic ground-state of the C_3 radical has already been reported.[14,15] Indeed, by using a functional form that has built-in the desired cusp behavior, it becomes rather trivial to model an accurate global single-sheeted form even when multiple conical intersections are present.[13,14] For this, one merely requires to define a parametric equation for the crossing seam in the space of internuclear distances $\{R_1, R_2, R_3\}$ (denoted hereinafter as **R**-space). For example, a line along a crossing with C_{2v} symmetry would be modeled as $\{t, t, f(t)\}$. We should next recall that the energy of the two crossing adiabatic sheets must (by definition), in the vicinity of the locus of intersection, vary

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