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On the Landau–Zener approach to nonadiabatic transitions for a vertical conical intersection

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Abstract

A Landau–Zener approach for nonadiabatic transitions in a vertical double cone conical intersection (CI) system due to Alijah and Nikitin [A. Alijah, E.E. Nikitin, Mol. Phys. 96 (1999) 1399] is pursued in terms of a rate constant perspective. Comparison of model results with those of surface hopping trajectory calculations shows that an approximate rate description for the upper cone population decay gives a reasonable global account of the nonadiabatic dynamics, especially when averages over a distribution of initial conditions is considered. Some limited results are also presented for the more general case of a tilted CI, and it is shown that concepts useful for the vertical CI also prove useful for this more complex situation.

Keywords: Conical intersection; Nonadiabatic transitions; Landau–Zener

1. Introduction

For photochemical reactions, conical intersections (CIs) often provide a "funnel" for efficient ultrafast passage from a photochemically accessed excited S1 state to the ground electronic state S0, thus governing nonadiabatic transition rates as well as branching ratios between ground state reactants and products; some recent reviews and books include [1–8]. CIs have been termed a sort of "Transition State" for photochemical processes [4,9], emphasizing their critical character for the S1 → S0 transition. While CIs have long been known in a chemical physics context focused primarily on small molecules in the gas phase, the appreciation of their importance in the wider arena of organic and biochemical photoreactivity is of more recent vintage [1,7,8]. Accordingly, there has been much important recent activity on CIs [1,4,7–9] especially for biomolecules, [6,8,10–12], with some activity for chromophores in solution [13–16]. Most such theoretical studies are quite heavily computational, involving challenging electronic excited state calculations in multiple coordinates, and various dynamical descriptions [6–8,17–20] including the quantum aspects of the nonadiabatic transitions themselves. While much has been learned from these valuable (and indispensable) efforts, we have inaugurated a complementary approach to the CI problem in a condensed phase environment [21–24] that of a modeling, analytically based analysis to help to characterize and predict fundamental aspects of CI topology and dynamics, especially for the expected local environment's large impact upon them when there is significant charge rearrangement in the CI system and environment has a polar character. One important aspect not yet directly addressed in this analytic/modeling effort is a detailed analytic attention to the nonadiabatic transition dynamics and probability *per se*, which we could term the CI analogue of the well-known Landau–Zener (LZ) treatment for the one-dimensional avoided crossing problem [25–28]. A necessary preliminary to a treatment including an environment is that of the isolated two-dimensional vertical double cone CI problem. Teller [29,30] long ago

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suggested a generalization of the LZ formula for the rate of a CI nonadiabatic transition, but it is only more recently that Nikitin and co-workers [27,28,31–33] have made important contributions to the development of such a generalized analytic approach.

Indeed, as indicated within, the present work is heavily based on a portion of the work of Alijah and Nikitin [33]. Our primary goal is to examine whether simple model descriptions based on a LZ approach, especially when further approximated by exponential time decays, can give a useful approximate global description of the nonadiabatic CI dynamics in the approximation of classical motion of the nuclei and a surface hopping [34,18,33] description for the nonadiabatic transitions. To the extent that such an admittedly approximate description is successful, this can provide an initial reference starting point and guide for characterizing CI dynamics in problems of interest involving complex chromophores and environments occurring in condensed phases and biomolecular systems, not only in connection with the theoretical effort [21–24] mentioned above, but also with simulations and experiments.

The outline of the remainder of this paper is as follows. In Section 2, we briefly review the Nikitin formulation for the vertical double cone problem, together with a description of a generalization of those results as well as a shift of focus towards a rate constant for the nonadiabatic transition. Numerical investigations are undertaken in Section 3 to test the approximate formulae. Section 4 is devoted to some initial comments on the more general tilted double cone problem, while Section 5 offers concluding remarks.

2. Vertical double cone CI and nonadiabatic transition rate constant

In this section, we briefly review the treatment of Nikitin and co-workers, focusing on that of Alijah and Nikitin [33], and indicate our further studies and in particular our shift of focus towards a rate constant. Although the contributions of these authors for the two-dimensional vertical double cone CI problem have a wide range of facets [33], we restrict the brief presentation here to the classical limit for the nuclear motion, a choice motivated by its comparative simplicity and the widespread use of nuclear classical mechanics in connection with surface hopping techniques [34,18].

2.1. LZ formulation

For present purposes, the first key feature of the classical Alijah and Nikitin (AN) treatment is the conversion to polar coordinates r and θ, where the radial coordinate r has its origin at the CI intersection point, such that the Hamiltonian is

$$H = \frac{p_r^2}{2m} + \frac{p_\theta^2}{2mr^2} \pm Fr. \tag{2.1}$$

for the radial motion in the effective potential energy $V_{\text{eff}}(r, L)$ comprising the rotational kinetic energy (with constant angular momentum $p_\theta = L$) and the potential energy contribution $\pm Fr$, with F being the constant magnitude of the potential energy slope. In this one-dimensional perspective, the connection to something like a one-dimensional LZ problem becomes quickly apparent. Thus, the representation Fig. 1b of the double cone system Fig. 1a indicates that the motion on the upper adiabatic surface is bound and periodic in r, and that the inner turning point r_i of the motion corresponds to a minimum spacing between the adiabatic states (dashed lines in Fig. 1b), and nonadiabatic transitions to the ground state may be approximated as occurring *solely* at this point.

Fig. 2 displays such a bound periodic motion in the upper cone, indicating that the trajectories are tangential to a circle around the cone apex, with the circle radius equal to the inner turning point r_i (note that the CI intersection point $r = 0$ is avoided). For sufficiently small angular momentum L, the trajectories at the assumed transition point are approximately straight lines and they describe an approximately hyperbolic potential energy profile, shown

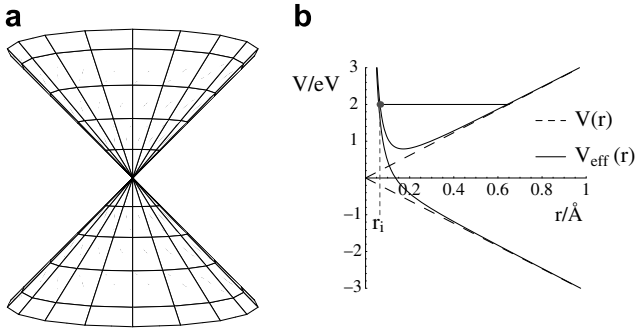

Fig. 1. (a) Vertical circular double cone potential surface. (b) Potential energy (dashed line) and effective potential (full line) for the double cone (Hamiltonian equation (2.1)) along the radial coordinate.

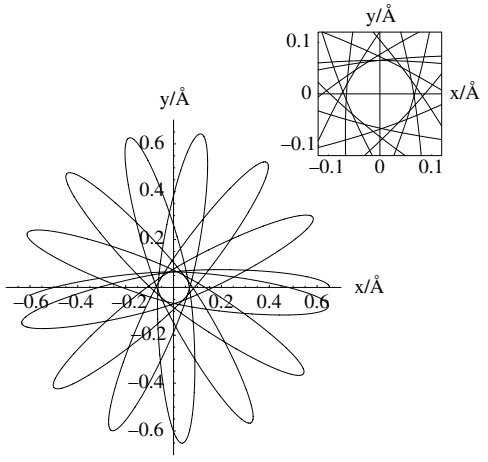

Fig. 2. Classical precessing trajectory on the upper cone of total energy $E = 2.0$ eV and angular momentum $L = 5.5\hbar$. Trajectories never reach the CI apex at $r = 0$ and are tangential to a circle of radius r_i. Inset shows the trajectory in the vicinity of the cone apex.