

Multidimensional dynamics and control in the vicinity of a conical intersection. A case study of the NO₂ molecule

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Electronic relaxation of excited electronic states of molecular systems is a key mechanism in several photo-chemical and photo-physical processes [1]. The different relaxation mechanisms from an excited electronic state are typically classified in terms of the presence of light emission. On the one hand, the relaxation can be very slow and in this case is usually accompanied by photon emission, e.g. spontaneous emission, fluorescence or phosphorescence. On the other hand, when light emission is not observed, the electronic relaxation is usually faster and due to non-adiabatic phenomena. Here, the excess electronic energy is converted into nuclear motion while passing through the funnel of a conical intersection, which occurs at nuclear geometries for which the electronic states intersect.

NO₂ is a prototypical molecule for which electronic relaxation due to non-adiabatic transitions is experimentally observed on the femtosecond time scale [2]. Following the relaxation path of the excited electronic state A²B₁ along the nuclear bending mode, electronic structure calculations have revealed [3] a conical intersection between the ground state X²A₁ and the first excited state A²B₁, occurring for all C_{2v} nuclear geometries. Since these two states belong to different representations of the C_{2v} symmetry, it is very important to consider the motion in the antisymmetric stretching, which breaks the C_{2v} symmetry, thus allowing the electronic relaxation.

We present our quantum chemical calculations featuring 2D potential energy surfaces of the electronic states X²A₁ and A²B₁ of the neutral molecule, as well as those of the most relevant electronic states of the cation in the photo-ionization process, both in the diabatic and the adiabatic representations. The corresponding transition dipole moments were also computed. With this information, we have obtained preliminary results, describing the nuclear dynamics upon excitation in the vicinity of the conical intersection. Moreover, applying an external field allows us to study the control of the dynamics by means of laser-induced couplings.

References:

- [1] N.J. Turro, *Modern Molecular Photochemistry* (University Science Books, 1991).
- [2] H.J. Wörner *et al.*, *Science* **334**, 208 (2011).
- [3] S. Sardar, S. Mukherjee, A.K. Paul, and S. Adhikari, *Chemical Physics* (2013). DOI:10.1016/j.chemphys.2013.02.006