

Nuclear quantum effects in excited state dynamics on high dimensional potential energy surfaces

Sandra Gómez, University of Vienna

Host: Graham A. Worth, University College London, g.a.worth@ucl.ac.uk

Cost reference number: COST-STSM-CM1405-36752

Period: 20/03/2017 - 07/04/2017

The main aim of this three week visit was to learn to use and start using the quantum dynamics method Multi Configurational Time Dependent Hartree, developed in the host group [1] with a final goal of identification of nuclear- spin isomers of the 1,1-Difluoroethylene molecule (molecule used before to show the difference in excited state dynamics of nuclear spin isomers in one dimension [2]).

Previously to the visit, two dimensional potential energies surfaces for the normal modes torsion/pyramidalization of CH_2 , torsion/pyramidalization of CF_2 , torsion/C-C stretching, C-C/pyramidalization of CH_2 and C-C/pyramidalization of CF_2 were obtained at the cc-pvdz/SA(3)-MS-CASPT2(2,2) level of theory. The first step of this project was to transform these adiabatic potential energy surfaces to an adequate diabatic basis to be used by MCTDH.

Although the shape of the potential energy surfaces suggest that the movement of the molecule in the excited state might only be dependent on the torsional mode, we decided to diabaticize not only with respect to that coordinate (which would show a bias towards this degree of freedom) but with respect to both of them for each mode/mode pair. For this purpose the propagation diabaticization method was used [3]. Due to the limited time available, only the torsion/ CH_2 pyramidalization potential energy surface could be converted to the diabatic picture for now, but the rest of them will be transformed and used in a near future.

Moreover, the initial conditions for the dynamics were calculated as the eigenfunctions of the ground state potential using the imaginary time propagation method. Due to the symmetric double-well shape of this surface, those eigenstates could be symmetric or anti-symmetric (both giving the same probability density distribution). Therefore, symmetric and antisymmetric initial wavefunctions were generated and approximated to bidimensional gaussians to spare computational time in the MCTDH calculation.

The collaboration started by this project will continue now that the functioning of the methods and their set-up was learned. Simulations on the diabatic potential energy surfaces using the MCTDH method with the calculated initial conditions (both symmetric and anti-symmetric) will be run in the near future and the obtained dynamics analyzed to conclude if the differences observed in one-dimension are palliated or enhanced in the presence of more dimensions. We also plan to extend the collaboration and try to distinguish between the isomers using the on-the-fly dynamics program *dd-vmcg*, developed in the group of Prof. G. Worth, thereby switching on all the degrees of freedom of the molecule.

-
- [1] M.H. Beck, A. Jäckle, G.A. Worth, H.-D. Meyer, *Phys. Rep.*, 324 (2000)
 - [2] S. Gómez, M. Oppel, L. González, *Chem. Phys. Lett.* (2017)
 - [3] G.W. Richings and G.A. Worth, *J. Phys. Chem. A*, 119 (2015)