SHARC – *ab initio* molecular dynamics with surface hopping in the adiabatic representation including arbitrary couplings

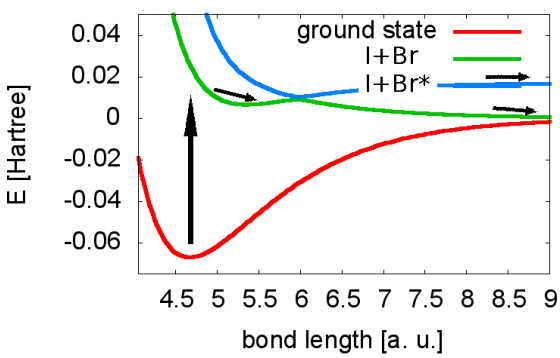
Martin Richter[1], Philipp Marquetand[1], Jesús González-Vázquez[2],

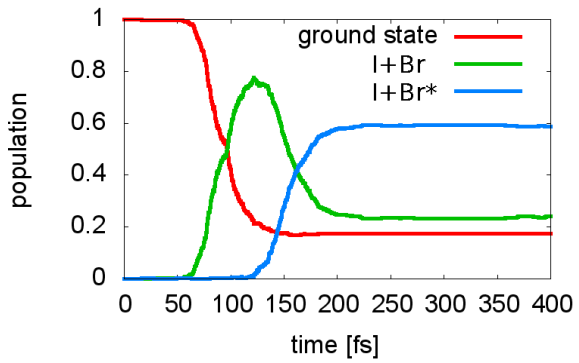
Ignacio Sola[2], Leticia González[1]

[1] *Institut für Physikalische Chemie, Friedrich-Schiller-Universität Jena, Helmholtzweg 4, 07743 Jena, Germany*

[2] *Departamento de Química Física I, Universidad Complutense, 28040 Madrid, Spain*

The **s**urface-**h**opping-in-**a**diabatic-**r**epresentation-including-arbitrary-**c**ouplings (SHARC) method is presented. This semiclassical molecular dynamics method allows for the inclusion of arbitrary couplings like spin-orbit coupling (SOC) or laser field induced couplings into molecular dynamical investigations. For this purpose, the surface hopping methodology [1] is extended and the couplings are incorporated into the system's Hamiltonian via a unitary transformation.





The method is tested in an analytically fitted 3-state system of IBr [2] (see left picture). Due to SOC there are two different dissociation channels, leading to I + Br($^2P_{3/2}$) (ground state) and I + Br*($^2P_{1/2}$) (excited Br) products.

To demonstrate the possibility of treating different couplings at the same time with high accuracy, the dissociation of IBr (including SOC) after excitation with a Gaussian shaped laser pulse (including field induced couplings) is investigated. The right picture shows, how the population of the different states changes with time due to the different couplings that affect the system's dynamics. These results, obtained from an ensemble of independent trajectories, are in good agreement with exact quantum dynamical calculations [3].

In contrast to quantum dynamics, within molecular dynamical calculations, the knowledge of the complete potential energy surface is not necessary a priori. Thus, the calculation of the required quantum mechanical properties can be done on the fly at the relevant geometries, allowing for the modeling of large and complex systems with many degrees of freedom.

[1] J. C. Tully, *J. Chem. Phys.*, **1990**, 93, 1061-1071.
[2] H. Guo, *J. Chem. Phys.*, **1993**, 99, 1685-1692.
[3] M. Richter, P. Marquetand, J. González-Vázquez, I Sola., L. González, *J. Chem. Theory Comput.*, **2011**, accepted.