

# Molecular dynamics with non-adiabatic and spin-orbit effects

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Molecular dynamics (MD) represents an important tool for modeling of the behavior of molecular systems in time. When applied to problems from photochemistry, a treatment of excited states and crossings between different potential energy surfaces has to be incorporated in the MD scheme. We present efficient techniques which allow to approximately compute the non-adiabatic couplings and perform surface hopping MD with CASSCF, MRCI, TDDFT, and ADC(2) methods. The performance of the non-adiabatic MD is illustrated on the examples of photoisomerization of azobenzene and internal conversion of excited adenine.

We present also surface hopping dynamics on potential energy surfaces resulting from the spin-orbit splitting, i.e., surfaces corresponding to the eigenstates of the total electronic Hamiltonian including the spin-orbit coupling. In this approach, difficulties arise because of random phases of degenerate eigenvectors and possibility of crossings of the resulting mixed states. Our implementation solves these problems and allows propagation of the coefficients both in the representation of the spin free Hamiltonian and directly in the “diagonal representation” of the mixed states. As a test case, we applied our methodology to deactivation of thiophene and selenophene in the gas phase, ethanol solution, and bulk liquid phase.

We also studied halogenated BODIPY derivatives, which are emerging as important candidates for photodynamic therapy of cancer cells due to their high reactivity in triplet states. Unsubstituted BODIPY has no phosphorescence activity, indicating no transition to triplets after excitation to a singlet state, while incorporation of heavy halogen atoms in its molecule makes BODIPY highly phosphorescent. It can be assumed that the presence of halogen atoms induces spin-orbit coupling resulting in a higher rate of intersystem crossing from the excited singlet state to the low lying triplet states thus leading the experimentally observed high phosphorescent activity. In order to fully understand the excited state dynamics of these systems regarding the influence of halogen atoms, we performed surface hopping molecular dynamics simulations including the spin-orbit effects.

## References

- [1] Plasser F., Crespo-Otero R., Pederzoli M., Pittner J., Lischka H., Barbatti M.: *J. Chem. Theor. Comp.* 10, 1395 (2014)
- [2] Pederzoli M., Pittner J.: *J. Chem. Phys.* 146 114101 (2017)