# VISTA Seminar

## Seminar 52

**May 24, 2023**

**10:00 am – 11:30 am EST / 3:00 – 4:30 pm GMT London / 4:00 pm – 5:30 pm CET Paris / 10 pm CST Beijing**

**TOC:**

# Ensemble density functional theory method for non-adiabatic dynamics of excited states

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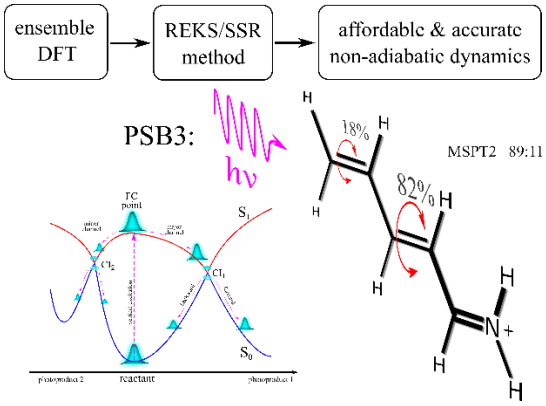


Ensemble density functional theory (eDFT), as developed in the works of E. Lieb[1] and E. Gross, L. Oliveira, and W. Kohn,[2] furnishes a rigorous framework for seamless inclusion of the nondynamic electron correlation into the description of ground and excited states of molecules. Having briefly introduced the basic formal aspects of eDFT, I will address implementation of practically accessible computational methodology capable of describing electronic states of molecules undergoing bond rupture, bond formation reactions.[3] Special attention will be given to the description of molecular properties in the ground and excited electronic states; in particular, the non-adiabatic couplings between the states, the forces on the nuclei, and the ionization energies. Several examples of application of the developed methodology to describe non-adiabatic reactions occurring in photochemical and photobiological systems will be given.[4]

**References**

[1] E.H. Lieb, ***Int. J. Quantum Chem***. **24**, 243 (1983)
[2] E.K.U. Gross, L.N. Oliveira, W. Kohn, ***Phys. Rev. A*** **37**, 2805 (1988); E.K.U. Gross, L.N. Oliveira, W. Kohn, ***Phys. Rev. A*** **37**, 2809 (1988); L.N. Oliveira, E.K.U. Gross, W. Kohn, ***Phys. Rev. A*** **37**, 2821 (1988)
[3] see *e.g.*, in M. Filatov, ***WIREs: Comp. Mol. Sci.*** **5**, 146-167 (2015);M. Filatov, ***Top. Curr. Chem***.: *Density-functional methods for excited states* **368**, 97–124 (Springer, Heidelberg, 2016)
[4] M. Filatov, S. K. Min and K. S. Kim, ***J. Chem. Theory Comput.*** **14**, 4499–4512 ( 2018); M. Filatov, S. K. Min and K. S. Kim, ***Mol. Phys.*** **117**, 1128-1141 (2019); M. Filatov, M. Paolino, S. K. Min and K. S. Kim, ***J. Phys. Chem. Lett.*** **9**, 4995–5001 ( 2018); M. Filatov, M. Paolino, S. K. Min, C. H. Choi, ***Chem. Commun.*** **55**, 5247-5250 (2019); M. Filatov, M. Paolino, R. Pierron, A. Cappelli, G. Giorgi, J. Léonard, M. Huix-Rotllant, N. Ferré, X. Yang, D. Kaliakin, A. Blanco-González, M. Olivucci, ***Nat. Commun.*** **13**, 6433 (2022).

# Spin-orbit coupling with relativistic MRSF-TDDFT as the first step for developing applications for studying intersystem crossings

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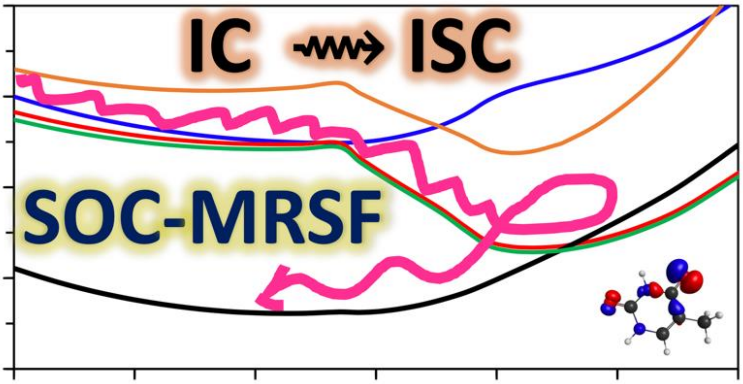


The Mixed Reference Spin-Flip TDDFT (MRSF-TDDFT) method, which solves the problem of spin contamination in multi-configuration electronic states, has been extended to calculate spin-orbit coupling (SOC) between singlet-triplet and triplet-triplet states using spin-dependent single-particle transition density matrices. Through benchmarks of atoms of groups IV and VI and organic molecules, the method shows sensitivity to the chosen basis sets and density functional, but with an average deviation of less than 10%.

SOCs obtained from MRSF-TDDFT follow El Sayed's rules, distinguishing between strong and weak spin-orbit couplings in organic systems. The calculated SOC-MRSF is consistent with the experimental and theoretical values in the spin-orbit energy splitting calculations for atoms even for the fifth-row element Sn. In addition, using SOC-MRSF, we can predict the expected intersystem crossing, for example, in thymine. Thus, due to its accuracy and ease of use, SOC-MRSF is a potential protocol for applications such as non-adiabatic molecular dynamics (NAMD) involving both internal conversions and intersystem transitions in large systems.

# How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 52
Time: May 24, 2023 10:00 AM Eastern Time (US and Canada)

Join Zoom Meeting
https://buffalo.zoom.us/j/94946130344?pwd=U0hvYkxVWWIrRXJlRjZDSWR6VWNGQT09

Meeting ID: 949 4613 0344
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