

# VISTA Seminar

## Seminar 41

**August 17, 2022**

**10:00 am – 11:30 am EDT / 3:00 – 4:30 BST / 4:00 pm – 5:30 pm Paris**

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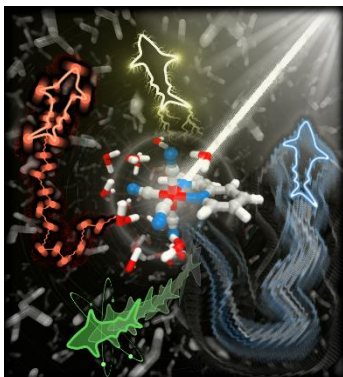
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## Unraveling the interplay of ultrafast electronic, spin, nuclear, and solvent dynamics in a solvated iron complex using the SHARC method

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The ultrafast photoinduced dynamics of  $3d$  transition metal complexes is a fascinating topic at the center of attention of several research fields, e.g., for applications as photosensitizers in dye-sensitized solar cells. In these dynamics, several interesting processes are at play simultaneously, such as charge transfer, intersystem crossing, or nuclear and solvent relaxation. In order to disentangle these processes in the prototypical iron complex  $[\text{Fe}(\text{CN})_4(\text{bipyridine})]^{2-}$ , we have simulated the photoinduced dynamics with all relevant electronic, nuclear, and solvent degrees of freedom [1] using the surface hopping including arbitrary couplings (SHARC) method [2]. To this end, we employ spin-orbit-coupled potential energy surfaces based on time-dependent density functional theory in combination with a hybrid quantum mechanics/molecular mechanics (QM/MM) computations.

In  $[\text{Fe}(\text{CN})_4(\text{bipyridine})]^{2-}$ , excitation in the visible range populates singlet MLCT states, which evolve within several hundred fs into metal-centered (MC) states via a reverse charge transfer process (yellow in the above figure). On a similar time scale, the complex undergoes intersystem crossing (green) from the singlet to the triplet manifold. The electronic evolution also affects nuclear motion, as the change from MLCT to MC states leads to considerable Fe–ligand bond lengths on a 100fs time scale (red). Most interestingly, we find as one of the fastest responses of the system the breaking of hydrogen bonds between the solvent water and the cyanide ligands (blue)—on a 40fs time scale after excitation. In summary, our simulations have provided a comprehensive picture of the sub-ps processes in this iron complex and the interdependencies between the system's degrees of freedom.

### References:

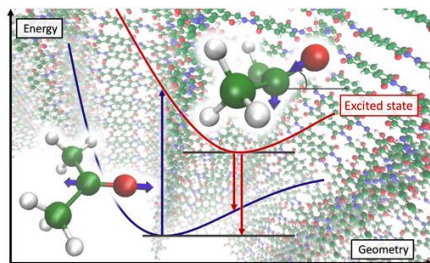
- [1] D. B. Zederkof, K. B. Møller, M. M. Nielsen, K. Haldrup, L. González, S. Mai: *J. Am. Chem. Soc.* 144, 12861–12873 (2022). <https://pubs.acs.org/doi/10.1021/jacs.2c04505>
- [2] S. Mai, P. Marquetand, L. González: *WIREs Comput. Mol. Sci.* 8, e1370 (2018). <https://wires.onlinelibrary.wiley.com/doi/10.1002/wcms.1370>

## Towards efficient excited-state dynamics with hybrid functional accuracy for large-scale periodic systems

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Conventional time-dependent density functional theory (TDDFT) or corresponding tight binding (TDDFTB) approaches represent a well-established standard for excited-state dynamics in material science, with high feasibility, robustness and increasing efficiency when going from conventional TDDFT to TB analogues. An accurate description of exact exchange is desirable for both methods, which however requires higher computational costs and is often still lacking for the computation of excited-state properties. Aiming for a pragmatic and efficient screening tool for the large-scale characterization of extended materials, we implemented two complementary approximate schemes with near hybrid functional accuracy in the CP2K program package [1,2], exploiting on the one hand the concepts of the auxiliary density matrix method (ADMM) [3] and on the other hand the idea of semi-empirical tight binding within the so-called simplified Tamm-Dancoff approximation (sTDA) [4]: Among the existing techniques to improve the unfavorable basis-set dependence and thus high computational cost of exact Hartree-Fock exchange, ADMM has proven to be a reliable approach to achieve significant speedups while retaining sufficient accuracy, being based on the idea of constructing an auxiliary density matrix for the evaluation of the exact exchange term and correcting the thereby introduced error with a density functional contribution. Efficiency can be even further increased with the semi-empirical sTDA ansatz, which was designed as a complementary excited-state approach for hybrid density functional ground-state references. In comparison to other tight-binding ansätze, sTDA has the advantage of relying only on global, atom-specific parameters requiring no pair-wise parameterizations and thus enabling broad applications. Employing semi-empirical electron-repulsion operators only introduces a minor loss in accuracy, in general smaller than 0.5 eV, but ensures that valence, charge-transfer and Rydberg excitations are equally well described by capturing the correct long-range asymptotics of exact exchange. We will motivate the use of these algorithms for efficient non-adiabatic molecular dynamics simulations, discuss specifics of the implementation in CP2K for periodic systems, required extensions for semi-empirical ground-state references as well as benchmarks and applications for periodic framework materials.

### References:

- [1] A.-S. Hehn, B. Sertcan, F. Belleflamme, S. K. Chulkov, M. B. Watkins, J. Hutter, *J. Chem. Theory Comput.* **2022**, 18, 4186.
- [2] T. D. Kühne *et. al.*, *J. Chem. Phys.* **2020**, 152, 194103.

## How to connect

Alexey Akimov is inviting you to a scheduled Zoom meeting.

Topic: VISTA, Seminar 41

Time: Aug 17, 2022 10:00 AM Eastern Time (US and Canada)

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103.122.167.55 (Australia Melbourne)

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