Seminar

■ **SPEAKER**
Dr. Yevhen Horbatenko (IBS CMSD)

■ **TITLE**
Optimization of newly developed Mixed-Reference Spin-Flip TDDFT method for its potential applications in luminescent and solar energy materials

■ **ABSTRACT**
The accurate description of the electronic excited states has become more important than ever, as theoretical modeling of the emerging materials, e.g., for photovoltaic, photochemical, and photobiological applications, strongly relies on the ability to correctly describe various types of electronic excitations. The linear-response (LR-) time-dependent density functional theory (TDDFT) is a widely used method for studying molecular excited states. However, it suffers from a number of well-known failures. Some of them can be corrected by the use of the spin-flip (SF-) TDDFT approach. However, its spin-contamination often impedes the identification of excited states as a singlet or a triplet. The newly developed, by some of us, mixed-reference (MR) SF-TDDFT method removes spin-contamination and provides the ease of identification of the excited states. We optimized the MRSF-TDDFT method for its potential applications for luminescent and solar energy harvesting materials. The prescriptions for the proper use of the method were formulated. Better accuracy of MRSF for the vertical excitation energies and the singlet-triplet gaps than that of widely used SF- and LR-TDDFT was demonstrated. It was shown MRSF can flexibly take both an implicit (via the XC functional) and an explicit (via double excitations) accounts of the electron correlation providing a more balanced description of various types of the excited states regardless of their character, whereas the accuracy of standard LR-TDDFT is limited by the XC functional. MRSF is capable of describing the multi-configurational electronic nature, the Jahn-Teller distortion, the violation of the Hund rule, and the potential energy surfaces of diradical(oid)s. Here, common LR- and SF-TDDFT theories fail. Also, MRSF described accurately a non-adiabatic coupling element, important for excited-state dynamics, not only between the ground and excited states of H2 but also the much more difficult to obtain coupling between the two excited states. The method accurately describes avoided crossing regions between the electronic states. A close agreement between MRSF and the MRCISD non-adiabatic coupling vectors for the case of polyatomic molecules was shown. We believe that the results obtained here will assist in establishing MRSF as a method of choice for computing a wide range of molecular systems for various photoapplications.

■ **DATE AND VENUE**
September 29, 2022 (Thursday, 15:30 - 16:30)
Seminar Room A (116)

■ **LANGUAGE**
English