Theory for Surface Processes and Spectroscopies Focus Topic

Room B116 - Session TH1-TuA

Electronic Structure Theory

Moderators: Robert Polly, Karlsruhe Institute of Technology, **Sefik Suzer**, Bilkent University, Turkey

2:20pm **TH1-TuA-1 Non-Orthogonal Configuration Interaction for the Study of Ground and Excited State Properties of Materials**, ***Ria Broer,*** University of Groningen, Netherlands*; C. de Graaf,* Universitat Rovira i Virgili and ICREA, Spain*; A. Sanchez-Mansilla,* Universitat Rovira i Virgili, Spain*; C. Sousa,* University of Barcelona, Spain*; T. Straatsma,* Oak Ridge National Laboratory, USA **INVITED**

The properties of materials including their interfaces and surfaces can be studied by a variety of advanced experimental techniques. The technique of choice depends on the material and on the property of interest. Likewise, a variety of theoretical/computational methods exist for the study of their ground and excited state properties and the method of choice again depends on the specific problem. In many cases progress in the understanding of the properties has leaped forward thanks to productive interaction between experimentalists and theorists. For such understanding the accurate computational reproduction or prediction of data is necessary but not sufficient, we need also interpretation in terms of (preferably simple) physical/chemical concepts.

This presentation introduces the non-orthogonal configuration interaction (NOCI) method, where the wave function of a molecular electronic state is written as an expansion in terms of a small number of many-electron basis functions (MEBFs),each representing a leading electronic configuration that is expressed in terms of its own, optimized orbitals. The MEBFs are single- or multi-configuration self-consistent field (SCF or MCSCF) wave functions. The orbital sets of different MEBFs are neither identical nor mutually orthogonal and this non-orthogonality complicates the computation of off-diagonal hamiltonian elements in the CI matrix. NOCI can be used to study isolated molecules, but also, when combined with the embedded cluster material model, to describe (rather) localized processes, like core excitations, in materials.

In the past decade we have extended the NOCI method to enable application to *ensembles* of molecules or fragments: NOCI-F. [1] The MEBFs are then spin-adapted linear combinations of anti-symmetrised *products* of MCSCF wavefunctions for each molecule/fragment in the ensemble. NOCI-F allows for the study of processes where inter-molecular (or inter-fragment) electron transfer or excitation transfer plays a role.

NOCI and NOCI-F are not computationally simple, but since the final wave functions are short expansions in terms of well-defined molecular states, a clear interpretation in terms of local excitations, charge transfer, etc. can still be given. It is shown how NOCI-F can be used to study multi-exciton generation and magnetic interactions in molecular crystals and electronic excitations involving (molecules on) surfaces.

[1] T. P. Straatsma, R. Broer, A. Sánchez-Mansilla, C. Sousa, and C. de Graaf, GronOR: Scalable and Accelerated Nonorthogonal Configuration Interaction for Molecular Fragment Wave Functions, J. Chem. Theory Comput. 18, 3549–3565 (2022)

3:00pm **TH1-TuA-3 Enabling Long Time-scale Quantum Molecular Dynamics Simulation for 5f-elements**, *P. Yang,* ***Enrique Batista,*** *M. Cawkwell, D. Perez,* Los Alamos National Laboratory **INVITED**

5f-element chemistry in solution is very intricate in nature.There is a pressing need to develop molecular dynamics (MD) methods that can describe quantum mechanical behavior, such as bond breaking and forming, at long timescales. Current first-principle MD methods can only reach tens of picoseconds, while classical force fields cannot accurately describe bond breaking and forming. To achieve this goal, we developed semiempirical density functional theory tight-binding (DFTB) parameters for 5f-elements that enable MD simulations at long time scales. Such simulations will be instrumental in understanding the evolution of speciation and reaction mechanisms.In this talk, we will share our recent development on a hybrid model that combines modern machine learning approaches with physics-based methods. We will demonstrate the transferability of this hybrid model on prediction of molecular structural parameters of various molecular clusters and a variety of chemical reaction free energies. Using these parameters, we also demonstrate microsecond-long quantum-MD simulations of nanoparticle systems for complex f-elements, shedding light on their dynamics and kinetics.

Author Index

Bold page numbers indicate presenter