

MO 6: Theory

Time: Tuesday 10:30–12:00

Location: MO-H7

MO 6.1 Tue 10:30 MO-H7

Unsupervised learning as a key tool to explore elements of the efficiency of PS1 in an QM/MM approach — ●FERDINAND KISS, SEBASTIAN REITER, and REGINA DE VIVIE-RIEDLE — Department of Chemistry, LMU Munich, Germany

Modern photovoltaic materials can be seen as biomimetics of photosynthesis in photoautotrophic organisms. Photosystem I (PS1) has one of the highest conversion efficiencies of 88%, from absorbed quanta to the reduction of NADP⁺. A deeper understanding of the effects of structural relations and electrostatic influences on the site energies, low-lying charge transfer states and absorption profiles of photoactive components of the PS1 promises to yield the answer to its outstanding efficiency. We developed an automated protocol for data extraction and processing from MD simulations by unsupervised machine learning. On this basis we set up electronic structure investigations in a QM/MM approach. Our maxim of a bias-free, dimensionality reduced and thus computational affordable approach to QM/MM studies aim towards a post-classical description of processes in large complex systems. With the developed tools at hand, we were able to rationalize relevant structural parameters in the 288 chlorophylls of the PS1 trimer. Furthermore, we were able to approximate electrostatic embedding in different pockets within the PS1 with minimal computational cost. The protocol as mentioned above and its results will guide the understanding of photosynthesis. The insights will help in the development of novel artificial photosynthesis designs.

MO 6.2 Tue 10:45 MO-H7

A Shortcut to Self-Consistent Light-Matter Interaction and Realistic Spectra from First-Principles — ●CHRISTIAN SCHÄFER and GÖRAN JOHANSSON — Department of Microtechnology and Nanoscience, MC2, Chalmers University of Technology, 412 96 Göteborg, Sweden

Nanoplasmonic and optical cavity environments provide a novel handle to non-intrusively control materials and chemistry. We introduce here a simple approach how an electromagnetic environment can be efficiently embedded into state-of-the-art electronic structure methods, taking the form of radiation-reaction forces [1]. We demonstrate that this self-consistently provides access to radiative emission, natural linewidth, Lamb shifts, strong-coupling, electromagnetically induced transparency, Purcell-enhanced and superradiant emission. As an example, we illustrate its seamless integration into time-dependent density-functional theory with virtually no additional cost, presenting a convenient shortcut to light-matter interactions.

[1] C. Schäfer and G. Johansson, arXiv:2106.07507 (2021).

MO 6.3 Tue 11:00 MO-H7

Novel trimer states in long-range atom-ion Rydberg molecules — ●DANIEL BOSWORTH^{1,2}, FREDERIC HUMMEL¹, and PETER SCHMELCHER^{1,2} — ¹Zentrum für Optische Quantentechnologien, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany — ²Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Luruper Chaussee 149, 22761 Hamburg, Germany

Recent theoretical works [1,2] predict p-state Rydberg atoms can form stable dimers with ions, defining a new class of long-range atom-ion Rydberg molecules. In these molecules, the binding arises from avoided crossings between attractive and repulsive polarisation potentials. Observation of these molecules was subsequently confirmed in [3].

We build upon these latest discoveries by studying the interaction between an ion and a *classic* ultra-long-range Rydberg molecule (ULRM). We introduce a third, ground-state atom and calculate Born-Oppenheimer electronic potential energy surfaces (PES) for the three nuclear species. The PES support three-body vibrational bound states, including both linear and non-linear nuclear arrangements. Estimates for the lifetimes of these trimer states are derived from decay rates to neighbouring PES, obtained using Landau-Zener transition probabilities. This work opens up a fresh avenue of investigation on the interaction of ions with ULRMs.

[1]: A. Duspayev et al., Physical Review Research, 3, 023114 (2021)

[2]: M. Deiß et al., Atoms, 2021, 9(2), 34

[3]: N. Zuber et al., arXiv preprint arXiv:2111.02680 (2021)

MO 6.4 Tue 11:15 MO-H7

Explicitly correlated wave functions for electron-positron interactions in atoms and molecules — ●JORGE CHARRY, MATTEO BARBORINI, and ALEXANDRE TKATCHENKO — University of Luxembourg, Luxembourg, Luxembourg

Positrons are capable of forming metastable states with atoms and molecules before the electron-positron annihilation process[1]. Such metastable matter-positron complexes are stabilized by a variety of mechanisms, which can have both covalent and non-covalent character. The study of these systems represents a challenge for quantum-chemical methods due to the need to describe the strong attractive correlation effects, which are limited by the employment of atom-centered basis sets to describe the positronic orbitals. In this work, we present a robust variational ansatz based on a combination of an electronic determinant, electron-positron pairing orbitals, and a Jastrow factor to explicitly accounts for the electron-positron correlations in the nuclear field, which are optimized at the level of variational Monte Carlo (VMC). We apply this approach in combination with diffusion Monte Carlo (DMC) to calculate binding energies for a positron e^+ bound to a set of neutral and anionic first-row atoms. To assess our approach for molecules, we study the interaction potential of the previously reported [2] system of two hydrogen anions H^- mediated by a positron ($H^- \cdot e^+ \cdot H^-$). We demonstrate the reliability and transferability of our correlated wavefunctions with respect to state-of-the-art calculations reported in the literature. [1] G. F. Gribakin, et al., Rev. Mod. Phys 82, 2557 (2010). [2] J. Charry, et al., Angew. Chemie 57, 8859 (2018)

MO 6.5 Tue 11:30 MO-H7

Non-adiabatic dynamics within the cavity-Born-Oppenheimer approximation — ●THOMAS SCHNAPPINGER and MARKUS KOWALEWSKI — Department of Physics, Stockholm University, Sweden

As shown by experiments, strong coupling between light and matter can be used to modify chemical and physical properties. In the case of a molecular system interacting with the vacuum field of a cavity, strong coupling reshapes the potential energy surfaces forming hybrid light-matter states, termed as polaritons or dressed states. In this way, it is possible to manipulate the non-adiabatic dynamics of the molecule and open new photophysical and photochemical reaction pathways.

A theoretical approach to describe such coupled molecular-photon systems is the so-called cavity-Born-Oppenheimer (CBO) ansatz. Analogous to the standard BO approximation, the system is partitioned and only the electronic part of the system is treated quantum mechanically. This separation leads to CBO surfaces depending on both nuclear and photonic coordinates. The interaction between different CBO surfaces can be formulated in terms of non-adiabatic coupling elements. In this work we combine the CBO ansatz with the complete active space self-consistent field (CASSCF) method, to describe the cavity-induced effects on ground and excited states as well as the non-adiabatic couplings. Based on the CBO-CASSCF results we perform nuclear wave packet dynamics to describe the non-adiabatic processes within the framework of the CBO approximation for a molecular-photon system.

MO 6.6 Tue 11:45 MO-H7

Inelastic H_2+H_2 , H_2+HD and $HD+HD$ collisions in the framework of a quantum-mechanical close-coupling approach — ●RENAT A. SULTANOV — Odessa College, Department of Mathematics, 201 W. University Blvd., Odessa, Texas 79764, USA

Molecular energy transfer collisions such as H_2+H_2 , H_2+HD , $H+H_2/HD$ and $HD+HD$ will be discussed and the results for the cross sections and thermal rate coefficients will be presented. Different H_4 potential energy surfaces (PESs) have been applied in the framework of a pure quantum-mechanical close-coupling approach [1]. The hydrogen-hydrogen atomic and molecular collisions play an important role in the astrochemistry of the early universe. In the case of the HD collisions it would be necessary to modify existing pure hydrogen H_4 PESs by shifting the center of mass of H_2 to HD. It was done in the framework of two different methods [2, 3]. However, these alternative procedures can provide quite different results for the rotational energy transfer cross sections. Physical and geometrical reasons of these differences will be discussed in our presentation. One of our methods for H_2-H_2 potential modifications [2] have been applied in [4,5].

1. R. A. Sultanov et al., *Chem. Phys. Lett.* **436**, 19 (2007).
2. R. A. Sultanov et al., *AIP Advances* **2**, 012181 (2012).
3. R. A. Sultanov et al., *J. Phys. B* **49**, 015203 (2016).
4. N. Balakrishnan et al., *Astrophys. J.* 866:95 (2018).
- 5 Y. Wan et al., *MNRAS* **488**, 381 (2019).