The aim of the **ATTONEW** project was to examine, from a theoretical point of view, the mechanism of charge transfer (CT) process in a molecular collision, taking place in the femto- (1 *fs*=10^{-15} s) or atto-second (1 *as*=10^{-18} s) time scale. The investigation of such a mechanism in real time is a pioneer application in the newly born field of Attochemistry. Domains like molecular electronics, bioinformatics and cancer research should benefit in the long-term from a detailed understanding of the CT process.

As an example, the collision of carbon ions C^{q+}(q=2,4) with the RNA base Uracil was considered. To study this process a novel time-dependent wavepacket method was developed. State-of-the-art quantum chemistry methods were merged with wavepacket propagation approaches, allowing for the real time investigation of the mechanism of CT in the proposed systems (Fig. 1). In the low-energy range of [1-10] eV, the collisional process can be described as the evolution of a quasi-molecule formed from the ion-molecule system in which the reaction coordinate corresponds to the distance R between the centre of mass of Uracil and the colliding carbon ion. In a first step, the study of the CT mechanism necessitates the calculation of the potential energies of the states involved in the process, as well as the couplings between these states. These are obtained using high level *ab initio* quantum chemical methods. In the second step, the time-resolved aspects of the ultrafast collision are to be studied using time-dependent wavepacket formalisms. One- (1D) and two-dimensions (2D) scenarios can be set up, which allow, among others, the calculation of the explicit time evolution of the electronic charge. The electronic density of the system allows to follow the charge exchange mechanism in real time.

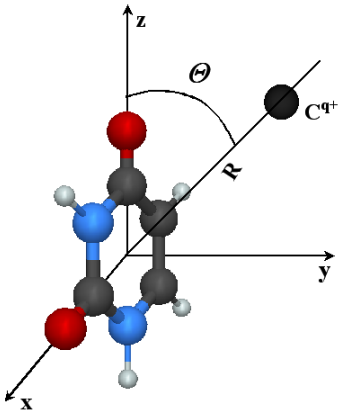


Fig 1. Molecular model of the C^{q+} + Uracil collision

The work plan of **ATTONEW** was divided into two levels, so that it includes the development of time-dependent theories to study the ultrafast dynamics of CT processes and its application to ion-biomolecule collisions. Concerning the development of methods, we have proposed two fundamental approaches to study the dynamics of a collision. First, the description of the nuclear wavepackets is simulated assuming that the electronic character of the system changes along the reaction coordinates. Second, the nuclear wavepackets dynamics is implemented assuming that the electronic character of the system does not change along the reaction coordinate.

Regarding the application level, 1D calculations for C^{2+} and C^{4+} collision with Uracil molecule by means of Complete Active Space Self Consistent Field/ Multireference Configuration Interaction methods have been done. A very large number of states (24) have been calculated, so that the entrance channel is included besides a reasonable number of exchange channels. The complexity of the system was patent from the strong interactions among a large number of states. Time-dependent wavepacket propagations have been performed, which allowed to simulate the CT process in the ultrafast time domain. In the 1D collision model we only considered the internuclear distance between the incident Uracil molecule and the carbon ion taken as the origin of electronic coordinates (with the impact parameter b=0).The 2D calculations have been performed including the distance R and the scattering angle θ, which allows to consider impact parameters between [0-20] a.u. Following these crucial results, the angular distribution of the projectile for a given scattering angle θ and a given time *t* has been obtained.

One of the major achievements of the **ATTONEW** project was to visualize for the first time the 3D electronic density in real time in the CT process. In this way, the importance of both projectile and target electronic structure in the collision has been proven. By following the nuclear motion and observing changes in the electronic density in time, we highly contribute towards a deeper understanding of this process in biological systems.

Understanding the ultrafast dynamics of CT process in an ion-atom collision system is enormously helpful to interpret the mechanism in systems of great complexity as C^{2+} and C^{4+} with Uracil. Therefore, the development of time-dependent theories was first implemented using a smaller (and from the computational point of view cheaper) model of a ion-atom

collision: S^{3+}+H. For this model, potential energy surfaces in 2D and corresponding couplings have been computed. For the sake of illustration, we regarded only the lowest five states of $^1\Pi$ symmetry. As an example, snapshots at t=75 fs of the wavepacket in 2D for the ion kinetic energy 10 eV are presented in Fig. 2. The evolution of the global electronic density in time is shown in Fig. 3.

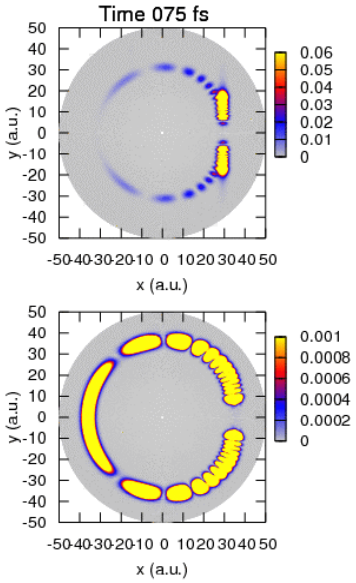
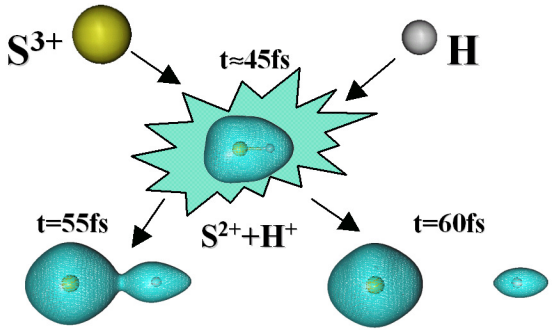


Fig.2 2D snapshots at t=75 fs of the wavefunctions in the entry channel with the $S^{3+}(3s^23p)^2P°$+H configuration (top) and the $S^{2+}(3s^23p3d)^3P°$+H^+ state (bottom).

Fig. 3. Snapshots of the time evolution of the global electronic density in the collision $S^{3+}(3s^23p)^2P°$ + $H(1s)^2S$.



Following this methodology, in the **ATTONEW** project the evolution of the nuclear wavepacket and the electronic density in the *fs* time scale in the context of ion-biomolecule collisions at eV energies has been presented for the first time. Such simulations allow a direct investigation of the dynamics for the proposed system and provide a detailed picture of the CT mechanism. Moreover, these studies are essential for the understanding of radiation effects in biological systems, where e.g. highly charged carbon ions are used for cancer radiation therapy. A wide range of the communities involved in this field of studies may be interested of the results obtained in **ATTONEW**.

Major results of **ATTONEW** have been published or are on the way to publication in scientific journals of high impact. Moreover, the work has been presented in different international conferences. Besides the scientific training objectives, Dr. Marta Łabuda has been involved in other activities inside the group of Prof. Leticia González, providing her the possibility to become a highly qualified scientist in the new field of attoscience and theoretical chemistry. All of experience gained during the fellowship (published results, collaboration and participation in scientific conferences) will make her capable of achieving a competitive career as an independent scholar, supervising and supporting other young researchers.

Summarizing: during the MC Fellowship Dr. Łabuda has been skilled in the development of state-of-the-art quantum chemistry and reaction molecular dynamical methods as well as in their applications in systems of different size and complexity. The multidisciplinary character of the project has integrated different concepts from chemistry, physics and biophysics, which we expect will lead to promising results and fruitful co-operations. It is believed, that our calculations will open a new line of research and motivate experimental investigations in the field of Attochemistry.

Contact

Dr. Marta Łabuda
e-mail: marta.labuda@uni-jena.de
Friedrich Schiller Universitaet Jena
Institut f. Physikalische Chemie
Project website: http://www.theochem.uni-jena.de/attonew/