FINAL PUBLISHABLE SUMMARY

The aim of ElectronStopping has been furthering our understanding of the processes triggered by ion projectiles when travelling through different kinds of matter by means of computer simulations. It is motivated by the need to improve our understanding of radiation damage in contexts such as nuclear materials (structural materials in fusion or fission plants, host materials for nuclear waste dilution and storage), materials for aerospace industry (susceptible under cosmic ray irradiation), and living tissue (for understanding radiation damage and improving cancer ion radiotherapy). There are both adiabatic and non-adiabatic effects of importance in radiation damage events. The former relate to projectiles of low velocity, typically under 0.1 atomic units (a.u.), i.e. 0.1/137 times the speed of light, and they produce nuclear displacements and chemical alterations but no electronic excitations. The latter are produced by faster projectiles and generate substantial electronic excitation, which significantly affects the damage. The main objectives of ElectronStopping are the first-principles simulation of non-adiabatic effects for ions moving through inorganic materials, and the adiabatic and non-adiabatic effects of ions moving through water and hydrated small biomolecules representative of key components of living tissue. The non-adiabatic simulations are performed with time-dependent density-functional theory for the electron dynamics and Ehrenfest dynamics for the nuclei, while the adiabatic simulations are based on first-principles molecular dynamics. The processes triggered in radiation damage events span several time and length scales. The present project has studied non-adiabatic effects for very short time scales, adiabatic atomistic effects at intermediate scales, and finally the connection to much larger scales by coupling first principles calculations to continuum simulations.

For inorganic materials, both metals and insulators were proposed, starting by systems that defy understanding but are experimentally well characterised. Hydrogen and Helium projectiles shooting through bulk germanium were studied in detail, for which very good recent data for both of them have been obtained by the group of Prof. Peter Bauer in Linz, Austria, the leading experimentalist in this kind of measurements. We calculated the electronic stopping power for H and He in Ge. The results for H have been very successful, reproducing the data, and offering information about the direction and impact-parameter dependence. Furthermore, the data – both experimental and computational – have been understood in terms of a simple model that captures the main effects, providing interesting insights onto the process. The computational results have been published [R. Ullah *et al*., Phys. Rev. B (2015)]. Simulations for He have also been performed, with mixed success: many experimental features were well reproduced and then understood, but an observed slope change in the stopping power versus velocity curve, analogous to what described previously for He projectiles in aluminium, has escaped both simulation and understanding. It is either beyond the fundamental approximations in the theory behind the simulations, or an effect related to the measurement itself. A joint theory-experiment paper is being finished for this system in which the agreements and discrepancies are presented very clearly, as challenge for further study, while proposing the hypothesis that the observed change in slope might be due to a smooth transition from effective conducing arbitrary projectile trajectories into channeling ones at low velocities (and thereby with smaller stopping) to the high velocity regime in which arbitrary trajectories of high stopping survive for long times [R. Ullah *et al*, to be submitted (2018)].

Simultaneously the effect of such electronic excitations on the interatomic forces has been explored for projectiles of larger atomic number (and higher charge), since their larger cross sections for both electron and nuclear scattering give rise to regimes in which the electronic and nuclear stopping are significantly coupled. A study of the alteration of forces by electronic excitation for Ni projectiles in Ni has been recently published [M. Caro *et al*. Sci Rep. (2017)], in which important alterations of adiabatic forces are observed, with behaviours quite different from the expectations used in empirical models of these effects (thermal spike, etc.). depicts iso-surfaces of deformation density, showing semi-core electron excitations with a defect of charge, and the tail, with an excess charge, which immediately allows to understand complicated alterations in effective interatomic particles. Furthermore, a second study for the Ni in Ni system [recently submitted to Phys. Rev. Lett, R. Ullah et al. arXiv.org (2018)], shows how the projectile's core electrons contribute very significantly (much more than the host's) to the magnitude of the electronic stopping power. Both studies provide important insights into how to model

radiation damage in systems with swift and heavily charged projectiles. A very interesting additional finding in the latter study has been that of a dynamical instability in the behaviour of the projectile's core electrons, which resembles the flapping of a flag under a steady wind. It contributes greatly to the energy transfer processes. Once observed, it makes a lot of sense. It has remained unnoticed, however, to the best of our knowledge, in spite of the century-long history of this problem. This is explained by the fact that the main paradigms for simulating electronic stopping assume a steady state; our numerical simulations do not.

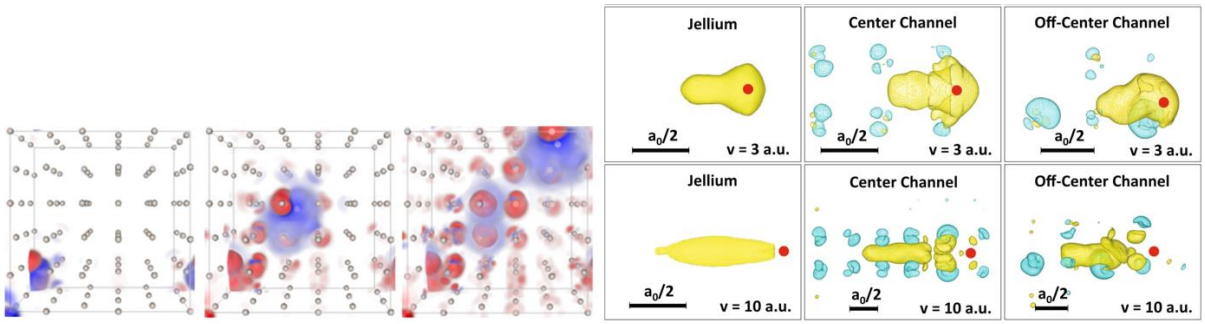

Figure 1. Deformation density isosurfaces for a Ni projectile in bulk Ni. The left three panels indicate negative (positive) deformation density with blue (red) for valence electrons [R. Ullah et al, arXiv (2018)]. The six panels on the right (blue/yellow), indicating the response of the semi-core electrons [M. Caro et al, Sci. Rep. (2017)].

From a formal point of view, the known expression of the equations of time-dependent density-functional theory in the frame of a moving basis set have been revisited from a differential geometry perspective. The nuclear motion produces a rotation-deformation of the basis set and a turning of the relevant Hilbert space when this is spanned by a basis set associated to the nuclear positions, as it is our case. The reformulation of the theory (in terms of tensors and covariant derivatives) has allowed us to get better insights and so propose new methods for the integration of the equations. A paper on this has been published [E. Artacho & D. O'Regan, Phys. Rev. B (2017)].

For the larger scale and longer time propagation of the excess energy, we have done preliminary explorations of multiscale modelling, coupling our first-principles atomistic simulations to continuum descriptions of mass and energy transfer through solids and liquids. In a first paper, first-principles molecular-dynamics simulations were used to follow the Hugoniot in the particular case in which a shock wave is triggered [O. Strickson et al, Phys. Rev. B (2016)], and in a second paper we used machine learning techniques for a more generic atomistic-continuum coupling [O. Strickson *et a*l, in preparation (2018)], both initially explored for bulk silicon.

Finally, in the line of exploring radiation damage of living tissue, a first study has been performed looking at the non-adiabatic damage of slow C2+ ions (up to 2.8 keV) in liquid water. Surprisingly, it has been found that most of the chemical damage (per unit length along the ion's trajectory), in terms of damaging chemical species produced, happens at the lowest energies explored (~0.5 keV). The mentioned species are mostly water molecule fragments (H and OH ions and radicals), but they also include the result of recombinations. Several of these species would produce chemical (mostly oxidative) end-damage in DNA. A paper on the matter has been published [J. Kohanoff & E. Artacho, PLoS ONE (2017)].

In summary, significant progress has been made in the understanding of radiation damage processes using first-principles simulations in regimes not directly amenable to pre-existing models of projectile stopping. The particular studies performed have been on paradigmatic chosen systems. The accomplished success shows a line of research into application of the methods used for systems of interest in different radiation damage contexts.