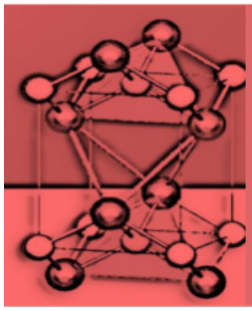

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Electronic stopping in liquid water, water vapor, and ice

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Time-dependent density-functional-theory (TDDFT) is a valuable tool to describe electronic excitations, in particular the energy loss to electrons and the electronic stopping power (S_e) in a material due to ion irradiation. TDDFT is implemented in two ways: linear response calculations (LR-TDDFT), and real-time electron dynamics simulation (RT-TDDFT). LR-TDDFT is used to compute the dielectric function and, from there, differential cross sections, energy loss function, and stopping power. Its main limitation is that electrons should respond linearly to the interaction with the external agent. This is valid at high velocities but becomes questionable as the velocity of the projectile decreases. RT-TDDFT, instead, is valid in any velocity regime and, while stopping power can be readily calculated, access to quantities like differential cross sections is far from obvious. Since the seminal work of Pruneda et al. 15 years ago [1], RT-TDDFT has been increasingly used to calculate electronic stopping power in a variety of materials including metals, semiconductors and insulators, 2D-materials, molecular systems, water and biological matter. The usual setup of these simulations is that the projectile crosses the sample at constant velocity and direction, exciting electrons along its way. Since the energy loss depends on the electronic density, which is non-uniform through the system, being this a crystal or a disordered medium, it is important to consider sufficiently many trajectories to obtain a meaningful average S_e that can be compared to observation. At low velocities the projectile is likely to get deflected from its path, and hence constant velocity is not meaningful any longer. Instead, Ehrenfest dynamics where the projectile (and the other atoms in the system) are allowed to move with the forces arising from the time-dependent density.

For disordered systems we recently proposed a trajectory pre-sampling method based on a geometric criterion, which proved very efficient for liquid water [2]. We will first summarize this methodology and discuss results for liquid water. Then, we will address the issue of additivity in stopping power of compounds in terms of their components, focusing on water vapor [2], comparing our RT-TDDFT curves to experimental and SRIM data and use them to validate Bragg's Additivity Rule (BAR) and the Core and Bond model for stopping in compounds [3]. For hexagonal ice we used a different sampling method using a grid of trajectories parallel to the hexagonal channels and studied it via Ehrenfest dynamics. This allowed us to unveil an interesting new effect by which low impact-parameter projectiles deposit energy into the target nuclei through the modification of the electronic density. Unlike standard nuclear stopping, this effect is maximum at the electronic Bragg peak, and explains an isotope effect between light and heavy water so far ignored [4].

Protons generate low-energy electrons that can also go on and interact with water, exciting other

and one must use Ehrenfest dynamics. Secondly, in principle they can exchange with the other electrons in the sample. Thirdly, at low velocities their quantum character cannot be ignored. At high velocities one can approximate this with classical electrons, but at low velocities this is not meaningful. The crossover is estimated to be at around 1 keV. The simulations with classical electrons are in progress, but in the meanwhile we have calculated the electronic stopping power for electrons using LR-TDDFT [5] and found that the effect of the mass is quite important, reducing S e significantly relative to protons. This reduction was traced back to energy and momentum conservation rules [6]. The location of the Bragg peak, however, is not reproduced well in linear response, while RT-TDDFT simulations are closer to experiment in this respect.

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