

## Structure and dynamics of exciton in hematite $\text{Fe}_2\text{O}_3$ semiconductor

L. Rassouli<sup>1</sup>, A. V. Akimov<sup>2</sup>, M. Dupuis<sup>1,3</sup>

1. Department of Chemical and Biological Engineering, University at Buffalo SUNY, Buffalo, NY, USA

2. Department of Chemistry, University at Buffalo SUNY, Buffalo, NY, USA

3. Computational and Data-Enabled Science and Engineering Program, University at Buffalo, SUNY, Buffalo, NY, USA

Photoelectrochemical cells (PECs) convert solar energy to fuel (chemical energy) as a form of a clean energy source. The mechanism of PECs comprises three main steps (1) light absorption and charge carrier (electron and hole) generation, (2) charge carrier transport, and (3) charge carrier utilization in interfacial redox reactions such as water oxidation (OER), hydrogen evolution (HER), overall water splitting (OWS), and others. This study focuses on the first step, the characterization of exciton structure, dynamics, and lifetimes based on the evolution of the electron-hole pair excited states in hematite  $\text{Fe}_2\text{O}_3$  as a prototypical system. Subsequently, excitons separate into charge carriers (electron and hole polarons) that become the surface redox-active species. Detailed knowledge of the characteristics of excitons as the result of light absorption can lead to the identification, design, and discovery of intrinsically better photocatalytic materials. We report here on the dynamics of excitons studied with the help of the non-adiabatic molecular dynamics approach as implemented in the open-source Libra package. The method describes the real-time dynamics of the electronic excited states at the time-dependent density functional theory (TDDFT) level considering electron-nuclear coupling effects. The calculations yield recombination times around 60 ps and 3000 ps from the first and second excited states, respectively. Our calculations are in good agreement with the detailed experimental XUV measurements of Leone's groups. We also address the question of charge localization in excitons as revealed by Baker's group XUV data, whereby the electron-hole pair is assigned to be separated by  $\sim$  a single M-O bond.