First-principles investigation of charged dopants, defects, and defect complexes in 2D transition metal dichalcogenides

Anne Marie Z. Tan[1], Christoph Freysoldt[2], Richard G. Hennig[1]

[1]Department of Materials Science and Engineering, University of Florida, Gainesville, FL 32611, USA

[2]Max-Planck-Institut für Eisenforschung GmbH, Max-Planck-Straße 1, 40227 Düsseldorf, Germany

Two-dimensional (2D) semiconductor materials, such as transition metal dichalcogenides (TMDCs), monochalcogenides, and phosphorene have attracted extensive research interests for potential applications in optoelectronics, spintronics, photovoltaics, and catalysis. To harness the potential of 2D semiconductors for electronic devices requires better control and understanding of impurities, defects, and dopants and how they control the carrier concentration, character, and mobility in 2D materials. Accurate determination of their formation energies, charge transition levels, and electronic properties is crucial for the selection of materials and choice of suitable synthesis and processing conditions to achieve the desired performance.

Density functional theory (DFT) calculations of point defects in solids is a mature field with a proven record of experimentally validated predictions. However, modeling charged defects in single-layer materials with common plane-wave DFT approaches poses additional challenges which lead to the divergence of the energy with vacuum spacing. Recently, Freysoldt and Neugebauer developed a correction scheme which employs a surrogate model to restore the appropriate electrostatic boundary conditions for charged 2D materials. We perform DFT calculations utilizing this correction scheme to accurately compute formation energies and charge transition levels associated with dopants, defects, and defect complexes in technologically relevant TMDCs such as MoS_2 and WSe_2. We identify dopants which can form defect complexes with intrinsic defects such as vacancies, acting as compensating defects and modifying the electronic properties of the individual defects. An example of this is the Re dopant – S vacancy complex in MoS_2 which we predict to be thermodynamically favorable and which has been observed experimentally. We also analyze the electronic structures of these defects to gain insights into their effect on bonding and magnetism in 2D TMDCs.