Formation energies of charged defects – resolution of long-standing difficulties

Sokrates T. Pantelides[1]

Blair Tuttle[1,2], Andrew O'Hara[1], Yuning Wu[3], and Xiao-Guang Zhang[3]

[1]*Department of Physics and Astronomy and Department of Electrical Engineering and Computer Science, Vanderbilt University, Nashville, TN 37235*

[2]*Department of Physics, Penn State Behrend College, Erie, PA 16563*

[3]*Department of Physics and the Quantum Theory Project, University of Florida, Gainesville, Florida 32611*

Formation energies of defects in semiconductors is an essential ingredient in the study of a wide range of semiconductor properties. For several decades, they have been calculated using supercells, but, for charged defects, the standard definition leads to a divergence that is removed by setting the average electrostatic potential to zero. Several techniques have been developed to further address inherent difficulties. These difficulties are exacerbated in 2D materials where unphysical electric fields appear in the vacuum regions, requiring new methods to remove them. Here we trace the origin of the divergence to the fact that the definition of charged-defect formation energies violates the principles of statistical mechanics for defects in semiconductors. Moreover, the *ad hoc* elimination of the divergence at each iteration in the self-consistency loop results in a potential and charge density that are not connected by Poisson's equation, i.e., self-consistency is compromised. We then describe a fundamental resolution of the issue that leads to a *new definition of charged-defect formation energies without a divergence or other difficulties*[1]: so-called "charged defects" are not truly charged -- a neutral defect releases a bound electron to the conduction bands or takes up an electron from the valence bands. The crystal is always neutral and for every "charged" defect, there is a neutralizing carrier in some band state (or elsewhere), i.e., the supercell is neutral and thus the entire crystal is crystal in agreement with physical reality. We show that the jellium definition can be derived from the new definition by invoking approximations whose validity cannot be assessed *a priori*, which sets up the new definition as a standard. Calculations for bulk materials reveal that the differences in the two approaches are relatively small, but for 2D materials, in particular BN, the differences can exceed 1 eV. Convergence with supercell size is as fast as for neutral defects.

1. Y.-N. Wu, X. G. Zhang and S. T. Pantelides, "*Fundamental resolution of difficulties in the theory of charged point defects in semiconductors*", *Phys. Rev. Lett.* **119**, 105501 (2017).