## Defect calculations for layered materials and their heterostructures

***M. Lorke, P. Deak, B. Aradi**, Bremen Center for Computational Materials Science, University of Bremen*

### In Short

- Semiconducting transition metal dichalcogenides are promising candidates for novel nanolaser and valleytronics devices
- Opto-electronic properties and degree of valley polarization under varying excitation conditions are of significant importance for actual device operation
- We investigate excitation-dependent valley polarization properties using state-of-the-art many-body methods

In this project we investigate defects in semiconducting two-dimensional transition metal dichalcogenides (TMDCs) with a focus on application in optoelectronic devices. To simulate realistic conditions, essential building blocks include the electronic and optical properties including the Coulomb interaction that is particularily strong in 2D materials. Lately the focus in this field has shifted from pure 2D monolayers towards layered heterostructures to gain flexibility in engineering the desired properties.

The work horse of theoretical defect physics is density functional theory (DFT). Earlier, local or semilocal approximations (LDA and GGA, respectively) were used for the exchange-correlation functional in the standard Kohn-Sham (KS) framework but, as the emphasis of research has shifted from microelectronics to optoelectronics and photovoltaics, i.e., from the traditional zinc blende and wurtzite semiconductors with relatively narrow gaps, to wide band gap materials of more complicated structure, it has become obvious that the inaccuracy of calculated defect properties, due to the electron self-interaction error involved with these approximations, is not tenable anymore. It has been shown that the use of the Heyd-Scuseria-Ernzehof (HSE) hybrid exchange functional, in the generalized KS-framework, allows the restoration of the correct piece-wise linear behavior of the total energy, as a function of the occupation numbers and, thereby, leads to highly accurate results for the electronic structure of defects in bulk semiconductors. However, the HSE hybrid is a semiempirical functional and, unfortunately, its two parameters are materials specific. Both parameters are connected to the description of electronic screening, so more transferability can only be achieved by improving the model used for the screening function $\varepsilon(q)$. Moreover, the screening $\varepsilon(q)$ introduced in the HSE functional is isotropic, hence it cannot accurately describe the strongly anisotropic screening in layered materials, let alone in monolayers. we have suggested a new, screened exchange functional based on the microscopic screening in the material, and have shown that, with one value of the only tunable parameter, it provides the proper behavior of the total energy for several related semiconductors and their alloys. This new screened exchange functional works for a wide range of bulk semiconductors with band gaps between 0.7 and 13.4 eV with a screening as shown in Figure 1. In this project we will extend this approach to spatially inhomogeneous situations, as found in layered materials. This extension is important, as we could show, that the parameters optimal in the bulk cannot provide the required piecewise linear behavior of the energy for monolayers offinite size, and break down completely for atomically thin 2D layers.

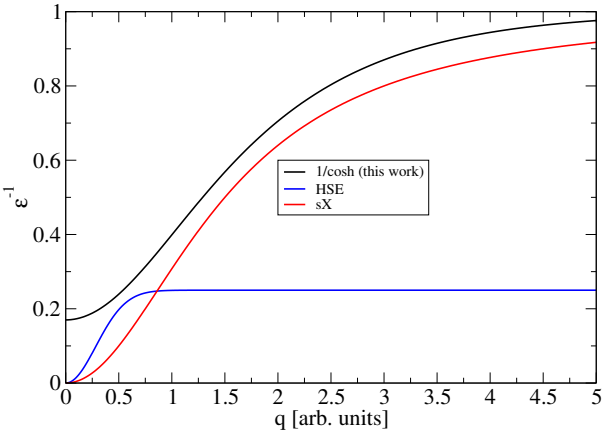


***Figure 1:** Novel screening functions $\varepsilon^{-1}(q)$ for GaN. For comparison the HSE hybrid and the sX functional are shown.*

The novel functional will allow for the investigation of the electronic and optical properties of defects in such structures and to gauge their application potential as dopants, light emission centers and centers for catalytic reactions. It will also increase the accuracy of calculating defects on semiconductor surfaces, allowing, e.g., a better modelling of photo-catalytic processes. The project is planned for at least two years, including both method development and application in practical defect studies. In the first year of the project, while method development is underway, we will focus on carrying out reference calculations to assist the method development by using the GW 0 approach These will be done in monolayers of GaSe, and transition-metal-dichalcogenides (TMDs). Equi-

librium geometries for the defects will be obtained using tuned HSE functionals, with parameters optimized to reproduce the single-particle gap and fulfill the generalized Koopmansâ theorem. Such parameters have been already found for GaSe, and will be determined for TMD materials. Since we have found that the electron distribution in bulk hBN and GaSe are relatively homogeneous, calculations on the intrinsic defects and dopants of bulk TMDs will be carried out using the HSE functional optimized for the bulk (or, alternatively, with the bulk version of our new functional). Also our earlier study on intrinsic defects of bulk GaSe will be extended to dopants and transition metal impurities.

## WWW

http://www.bccms.uni-bremen.de/

## More Information


[1] P. Deak, M. Lorke, B. Aradi, and T. Frauenheim, Optimized hybrid functionals for defect calculations in semiconductors, J. Appl. Phys. 126, 130901(2019).

[2] P. Deak, E. Khorasani, M. Lorke et al., Defect calculations with a hybrid functional in layered compounds and in slab models, Phys. Rev. B 100, 235304 (2019).

[3] M. Lorke, P. Deak, and T. Frauenheim, Asymptotically correct screened exchange potential for semiconductors: A Koopmanâs compliant approach. arXiv preprint arXiv:1907.08404, 2019.

[4] P. Deak, M. Han, M. Lorke, M. Farzalipour Tabriz, and T. Frauenheim, Intrinsic defects of GaSe, submitted.

[5] J. Klein, M. Lorke, et al., Site-selectively generated photon emitters in monolayer MoS2 via local helium ion irradiation. Nature Commun. 10, 2755, (2019).


## Project Partners

Center of Nanotechnology and Nanomaterials, Walter Schottky Institut and Technical University Munich, Munich, Germany