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Molecule-2D heterostructures - still a challenge for computational chemistry

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Low-dimensional materials have garnered significant attention due to their exceptional physical and chemical properties. Heterostructures consisting of such materials with specially designed molecules allows the finetuning of properties as a result of charge transfer, both via physisorption or covalent functionalization. We investigated two different types of 2D materials, graphene with its semimetallic behaviour and MoS2 as a semiconductor with strongly bound excitons. The interaction of these 2D materials with various electron acceptor and donor molecules as suitable n- and p-type dopants was studied. As a first outcome, graphite and bilayer graphene were investigated with the strong electron-accepting FeCl3 as an intercalant. Both the electronic and magnetic properties can be adjusted by different stacking sequences and by applied strain [1]. Furthermore, the intercalation of halogens in graphitic materials supports the formation of polyhalogen anions in confined space due to charge transfer. Additionally, chemical modification of the acceptor and donor molecules and their arrangements are investigated with respect to their doping affinity of graphene. The same acceptors and donors are also used for charge transfer to and from MoS2, where both single and double side functionalization was investigated [2]. With the careful selection of donors and acceptors on either side, an increase of the doping to MoS2 could be achieved. Double side covalent functionalization of MoS2 can control the electronic and the optical band gaps [3]. Depending on the choice of the chemical groups and their coverage, the electronic properties can be tuned from semiconducting to metallic and the optical band gap can be shifted by up to 1 eV. For all these calculations, a careful selection of the DFT functional applied, supercell size and computational parameters is necessary. Additionally, to get reliable results for electronic and optical band gaps, the GW method and the BSE approach has to be applied on top of the Kohn-Sham DFT results.

[1] J. Dai, S. Yadav, B. Paulus, C. 2023, 9(4), 95
[2] S. Ray, B. Paulus, Nanomaterials 2025, 15(3), 193
[3] K. Wang, M. Kapitzke, L. Green, B. Paulus, J. Mater. Chem. C 2022, 10, 6009