Charge transfer through functionalized 2D materials

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First principle investigations of two-sided functionalized 2D systems

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In Short

- Transition metal dichalcogenides
- Molecular functionalization
- Donor-acceptor pairs
- First principle calculations

Over the past two decades, two-dimensional materials (2DMs) have garnered significant attention, owing to the versatile nature of their atomically thin crystalline layers obtained from the exfoliation of the bulk form. These comprise an entire library of materials which are all beneficial in varied industrial applications, due to their excellent electronic and optical properties and the corresponding flexibility that originates from the modulation of such properties. Transition Metal Dichalcogenides (TMDs) are a member of the family of 2DMs with the chemical formula MX_2, where M is a transition metal belonging to group IV (Ti, Hf), group V (Nb, Ta) or group VI (Mo, W) and X is a chalcogen (S, Se). Owing to their sizable electronic band gaps, TMDs find a fascinating array of applications in optoelectronic devices, diodes, transistors, and semiconductor-integrated circuits. MoS_2, in particular, undergoes a notable transition from an indirect to a direct electronic bandgap of 1.8 eV when moving from its bulk form to the 2H phase monolayer [1]. Research over the past two decades has shown that incorporating molecular functionalities into the system through covalent or non-covalent functionalization schemes allows for the control of the physicochemical and optoelectronic properties of the 2DMs [2]. The phenomenon of surface adsorption or doping has a direct impact on the electronic structure of the system as a result of changes in charge carrier density.

This study seeks to conduct first-principle calculations to investigate the electronic structure of both one-sided and two-sided functionalized MoS_2 monolayers. In the case of two-sided functionalization, the goal is to observe the potential charge transfer through the TMD. In order to effectively characterize the electronic and optical properties of the material, it is important to note that calculations performed within the DFT framework, combined with a Generalized Gradient Approximation (GGA) functional such as PBE, tend to underestimate the electronic band gap. Therefore, single point calculations performed with short-range hybrid functionals such as HSE06 are expected to evaluate electronic properties of the system more accurately. To further address this issue, we will perform single-shot G_0W_0 calculation to adequately account for the screened Coulomb interaction. These calculations will enable the characterization of both pristine and variably functionalized MoS_2 with different pairs of donor and acceptor groups. Additionally, the Bethe-Salpeter Equation (BSE) will be utilized to estimate the nature and extent of exciton binding in the system, providing an improved understanding of the material's dielectric function and optical properties. It is also important to note that the charge transfer in the system is closely related to the adsorption structure of the donor and acceptor molecules on the TMD surface, hence it is necessary to describe the functionalized TMDs with a suitable dispersion correction scheme, such as DFT-D3 in this project. The insights obtained from these calculations can be used to design functionalized TMDs with a wide variety of donor and acceptor molecules and meticulously characterize their electronic and optical properties. This is illustrated in Figure 1 which shows the observed charge transfer in a two-sided functionalized 4 x 4 MoS_2 supercell, as calculated in preliminary work with respect to this project.

Method

All calculations will be performed using the Vienna *ab initio* simulation package (VASP) with a plane

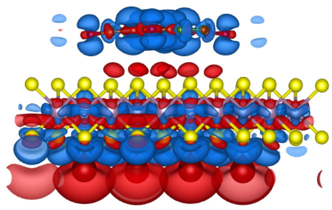

Figure 1: *Isosurface plot of charge density difference for two-sided functionalized MoS_2. F_4TCNQ molecule act as an acceptor on top and 4 Na atoms on the bottom are donors. Regions of electron density accumulation and depletion are represented in blue and red, respectively. Contour value : 0.001 e/Å^3*

wave cutoff of 500 eV. The valence electron-core ion interactions will be described using the projected augmented wave (PAW) method. Furthermore, interlayer interactions will be accounted for using Stefan Grimme's semi-empirical DFT-D3 correction scheme alongwith Becke-Johnson damping. The general workflow for studying structural, electronic and optical properties of the systems under consideration begin with structural relaxations performed at the DFT level with a PBE+D3 method. To evaluate electronic properties of the systems, density of states and band structure calculations will be done with a short-range hybrid functional such as HSE06. The atomic charges in the system will be estimated using a Bader charge analysis scheme. In order to account for electronic correlation, a single-shot G_0W_0 calculation will be performed. The excitonic effects in the system will be investigated by calculations based on the Bethe-Salpeter Equation performed at the DFT level with a suitable functional [3,4].

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https://www.bcp.fu-berlin.de/en/chemie/chemie/forschung/PhysTheoChem/agpaulus/index.html

More Information

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DFG Subject Area

327-01, 327-02