Ab initio ultrafast dynamics in hybrid inorganic-organic interfaces

Ab initio modelling of laser-induced ultrafast electronic dynamics in molecularly doped transition-metal dichalcogenide monolayers

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In Short

- Level alignment of transition-metal dichalcogenides/carbon-conjugated molecules hybrid interfaces
- Effect of hybridization in their electronic and optical properties
- Calculate their charge transfer dynamics in reciprocal space using RT-TDDFT

Hybrid donor-acceptor (D-A) interfaces formed by inorganic semiconductors doped by organic molecules have been considered as promising systems for novel applications in opto-electronics since a couple of decades. The advantage of these new materials resides in the combination of thes large carrier density and mobility from the inorganic component and the strong light-harvesting and emission characteristics of the organic molecules. Recently, the advent of two-dimenstional semiconductors, such as transition-metal dichalcogenides (TMDC), has further expanded the possibilities for realising hybrid interfaces. These new hybrid materials have attracted the focus from the community due to their peculiar electronic and optical properties12. Such systems exhibit interfacial charge transfer, which usually manifest itself already in the ground state, and it is one of the reasons for such vast applicability of these materials in (opto)electronics.

Despite the recent advances important aspects in these materials related to dynamical mechanisms of charge transfer in the ultrashort time window following a coherent perturbation are not fully clear and yet they are of crucial importance for applications. Initial steps have been taken in this direction by our group modelling a prototypical hybrid D-A model interface formed by a hydrogenated silicon nanocluster doped by the strong electron accepting molecule F4TCNQ 3. In that work, based on real-time time-dependent density-functional theory (RT-TDDFT) coupled with Ehrenfest molecular dynamics scheme, we have shown a non-trivial interplay between intramolecular and interfacial charge transfer driven by the electron-vibrational coupling building ip in the first 80 fs after a resonant laser excitation

In this project we want to extend this analysis to realistic interfaces formed by monolayer TMDCs doped by carbon-conjugated molecules. To this end, we want to make use again of RT-TDDFT to monitor the time evolution of electronic population in both real-space and reciprocal space, to access the role of hybridization and charge transfer between the TMDC and molecule. To obtain a realiable linear-response reference for this analysis, we plan to perform additional calculations baed on many-body poerturbation theory (MBPT) 4, including the GW approximation and the solution of the Bethe-Salpeter equation (BSE) in order to acces the quasi-particle electronic structure and the optical spectra including electronc-hole correlations, respectivelys.

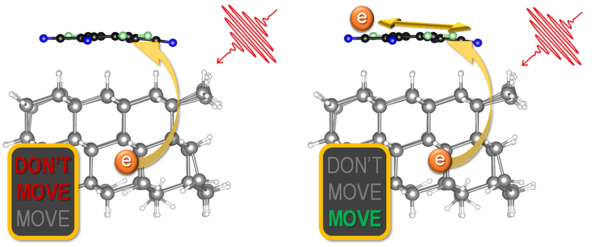

Figure 1: *Side view of the D-A hybrid interface formed by the H-Si(111) cluster doped by F4TCNQ. Left-side panel represents an electronic dynamics with the fixed atoms. This scenario discribe a interfacial charge transfer from the silicon cluster to the F4TCNQ molecule. Right-side panel represents the scenario where the atoms are allow to move. The coupling between the electronic and vibrational degrees of freedom induces a competition between interfacial charge transfer and intramolecular charge transfer. Images from Ref. 3.*

In preparation for the planned RT-TDDFT simulations, we explored the DFT band structure of a perylene@MoSe$_2$ heterostructure modelled in a 4x4 supercell. Since the description of the unit cell of MoSe$_2$ is lost in this approach, we applied an unfolding technique in order to project the band of the hybrid structure of those of the MoSe$_2$ unit cell (Fig. 2). The result presented in Fig 2 a) cleary indicates the presence of a mid-gap state corresponding to the highest-occupied orbital of the molecule. This is a favorable setup for (ultrafast) hole transfer. We additionally performed convergence tests on the linear absoprtion spectrum of the perylene@MoSe$_2$ interface and on the isolated MoSe$_2$ monolayer mod-

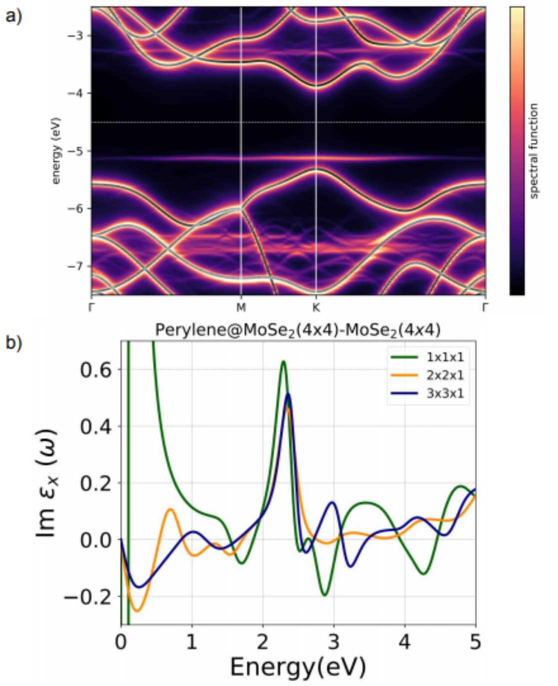

Figure 2: *a) Unfolded band structure of perylene@MoSe$_2$ calculated from DFT. The band structure of pristine MoSe$_2$ is superposed in grey shades, indicating the character of the states (black = Mo to white = Se). The dashed horizontal white marks the Fermi energy. b) k-point convergence of the RT-TDDFT optical spectra for perylene@MoSe$_2$*

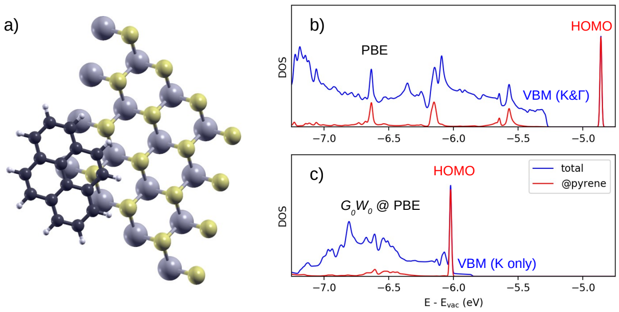

Figure 3: *a) unit cell of the pyrene@MoS$_2$(4x4) HIOS. b) density of occupied states, calculated with PBE. c) same as b), but with G_0W_0 correction.*

eled in the same supercell as the heterostructure, computed from RT-TDDFT. The result reported in Fig 2 b) shows that (i) a **k**-mesh of at least 3x3x1 points is necessary to capture the fine structures of the spectrum; (ii) the maximum at 2.25 eV can be assigned to a unique feature of the hybrid system: as such it is a good candidate for resonance pumping in the subsequent dynamical simulations. We also performed test GW calculations on the pyrene@MoS$_2$ heterostructure, a related system with less atoms (Fig. 3). For this system,significant differences between the valence density of states (DOS) calculated with DFT and GW can be seen. The GW correction lowers the energy levels of the heterostructure and, due to the different size of the shift for the molecule and the MoS$_2$, it gives rise to an altered band alignment.

In this project, we will investigate the charge-transfer dynamics of the perylene@MoSe$_2$ heterostructure modeled in a 4x4 supercell. In this analysis, we perturb the hybrid interface with an external laser pulse in resonance with the hybrid excitation at 2.25 eV and monitor the charge carrier dynamics in reciprocal space by projecting the time-dependent electronic states into the ground-state ones for a significant number **k**-points, which will give us crucial information about which states are involved in the excitation. The results obtained in this project are expected to serve as an important starting point when considering more complexes scenarios, e.g. the coupling between the vibrational and electronic degrees of freedom and, how this may affect the charge-transfer in such systems. In order to provide a reliable reference for these simulations, we will also perform MBPT calculations using the code Yambo 5, that offers excellent performance in terms of parallelization. RT-TDDFT calculations will be done using the real-space grid code OCTOPUS 6. This code offers an efficient parallel implementation for simulation molecular dynamics in extended systems and offers all the necessary features needed it to accomplish the goals of this project.

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More Information

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Funding

This work is funded by the German Research Foundation (DFG), projet number 182087777 - SFB 951, by the German Federal Ministry of Education and Research (Professorinnenprogramm III), and by the State of Lower Saxony (Professorinnen für Niedersachsen)