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7.11.2024, Garching, Garmany

Review of the PhD thesis presented by Mr Jakub Jasinski (l'Université de Toulouse III / U. Wroclaw) entitled "Control of the Excitonic Properties in Transition Metal Dichalcogenide based Structures"

Since the initial isolation of monocrystalline graphene in 2004 and the subsequent exploration, the palette of interesting materials has extended to include van der Waals semiconductors, such as transition metal dichalcogenides (TMDs). This thesis presents very interesting experimental investigations of methods to tailor the excitonic photophysics of TMD materials via intrinsic and extrinsic factors. In particular, the ability to tailor their properties is explored. This is done, for example, by patterning the substrate via interactions with proximal atomically thin layers, by creating hybrids consisting of heterostructures formed from TMD -2D perovskites and by applying local electric fields to manipulate the excitonic photophysics.

The thesis consists of six chapters spanning ~110 pages. It begins in **Chapter 1** with a helpful and very well-written introductory chapter that nicely defines the context for the thesis and summarises the current state of the art in the field. As expected, this chapter focuses on the family of TMD materials and the findings that dielectric screening can be strongly influenced via proximal interactions with atomically thin materials. It then continues to summarize the crystal structure and fundamental symmetries of TMDs, a topic that is needed to introduce their strongly layer-dependent electronic structure. Mr. Jasinski nicely boils down the significant body of literature to the most relevant publications, illustrating how valley and spin-dependent photophysics emerge from the strong spin-orbit coupling in TMD materials. Excitonic phenomena are introduced, a topic that permeates the experimental studies presented later in the thesis. Particular attention is paid to the impact of local and non-local screening and the formation of different optically bright and dark excitonic species and neutral and charged excitons, also variously discussed as polarons in the literature. In this context, the candidate rightly focuses on the spin and valley structure of the trions, biexcitons and higher-order excitonic complexes. The chapter then continues to present a

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summary of interlayer excitons in few-layer materials and the potential to tune their energy by applying static electric fields parallel to the stacking direction and the interaction of excitons and trions with a Fermi Sea induced by electrostatic doping. Beyond being a very useful summary of the current literature, Chapter 1 paints a picture of a very well-read student. It perfectly introduces the non-expert reader to the physics and optical properties of single and few-layer TMD-heterostructures. The thesis then continues in Chapter 2 with a concise summary of the experimental techniques applied, including linear reflectivity, (polarisation resolved) photoluminescence (PL), PL-excitation and Raman spectroscopy. The chapter discusses the capacitive model to describe the voltage-dependent carrier densities in gated structures. Again, the chapter balances the necessary details needed to understand the experimental results presented later in the thesis and the remaining brief. The experimental results in the thesis are summarised in Chapters 3-5. **Chapter 3** focuses on the study of anisotropic strain effects in MoS_2 monolayers exfoliated onto epitaxially prepared GaAs nano-templates. The local tensile strain is probed using Raman spectroscopy, as well as exciton and trion PL. Moderate strain levels of ~0.3-0.4% have been observed and a significant impact on the degree of polarisation is found. Interestingly, compelling experimental evidence has been found that the electron-hole exchange interaction is non-zero for the trion-like attractive polaron. These findings demonstrate how nano templating can be used as an additional control knob of the excitonic properties. Chapter 4 then continues to explore valley polarisation phenomena induced by a lesser-studied mechanism, namely, Dexter-like interactions that coherently couple same-spin states of the opposite valleys in k-space. When WSe2 monolayers are resonantly excited, the coherent exciton population in the excited state in one of the valleys is shown to be effectively transferred to the corresponding same-spin states of the opposite valley. This results in an inversion of the valley polarization. The candidate presents exciting experiments in which he performed PLE experiments with circularly polarised excitation and detection basis. Hereby, an inversion of the degree of polarisation is observed close to the B exciton when detecting the neutral and negatively charged biexciton transition. Good accord with the theoretical predictions is observed, strongly supporting the observation of Dexter transfer in the experiment. Complementary experiments in a WSe_2-metal halide perovskite heterostructure are also presented in which the type-II band alignment supports the formation of interlayer excitons. Again, a strong, substantial decrease or even inversion of the valley polarisation is observed when the polarised excitation is energetically resonant with higher-lying B exciton states. The results obtained are very interesting and well-described in the thesis. The final experimental chapter, **Chapter 5**, explores the electric field tuning of excitons in a natural $MoSe_2$ homo-bilayer that is double-gated to control carrier density and electric field. The results presented in this chapter are beautiful and represent how TMD multilayers can be used to explore fascinating many-body excitonic physics in such systems. Combining electric field-resolved reflectivity and photoluminescence with microscopic simulations reveals several different exciton types and opens the way to explore their mutual interactions. An avoided crossing is observed between the A_{1s} neutral exciton, and the inclusion of interlayer electron tunnelling could explain some of the interlayer states. For natural TMD bilayers, electron tunnelling was thought to be symmetry forbidden. The impressive results show that it occurs, presumably due to local symmetry breaking. The thesis concludes with a summary chapter, **Chapter 6**, that outlines the major results and sets them in the context of the available literature.

In summary, the thesis presents some beautiful spectroscopy of critical excitonic photophysical processes in TMD-heterostructures. It not only makes an excellent contribution to the body of literature, but it also contains some significant new findings. The results obtained have been published in six papers in high-quality journals, and I suspect that the results of Chapter 5 will appear in even more prominent journals due to their undoubted importance for the field. The applicant has presented his work at several international conferences, and I have no hesitation in recommending that the thesis be accepted as satisfying the requirements for a PhD. The quality of the results (especially Chapter 5) is superb, and the thesis and candidate are in the category for unique distinction.

Best regards,

Jonathan Finley