Chiral Optical Selection Rules for Electronic Quantum Control in Monolayer MoS_2

Ben Safvati

A fascinating new avenue for quantum information science involves the selective and dynamic population of degenerate but inequivalent extrema in the electronic band structure of certain kinds of crystals. For molybdenum disulphide (MoS_2), there exist two valleys at the corners of the Brillouin Zone conduction and valence band edges that behave as a two-level quantum-mechanical degree of freedom for charge carriers. These valleys, labeled K and K' in Figure 1, are opposite and highly separated in momentum space, providing resistance to scattering due to low-frequency defects in the crystal structure [1]. This makes the valley degree of freedom a powerful binary index for quantum electronic manipulation, similar to the spin of the electrons where modern devices are already using the quantum nature of spin to affect transport and storage properties. Spin-based quantum manipulation can be achieved through the use of magnetic fields, ferromagnetic point contacts, or other magnetic means that couple to the particles in the material and lead to spin-dependent interactions [2], but for the valley quantum number of electrons it remains an active area of research finding out how to control and populate individual valleys in a manner suitable for nanoelectronic devices.

Researchers at Columbia and Case Western University have demonstrated polarization of valley states in MoS_2 by utilizing the crystal symmetries of the material in a way such that the excitation of charge carriers in each valley can be highly contrasted. Using circularly polarized light with varying helicity, they found a valley-contrasted photoluminescence spectrum corresponding to long-lifetime excitations at each valley [3]. Although graphene-related valley technology has garnered the most theoretical interest, the visible-light band gap of MoS_2 and strong spin-orbit coupling of the d orbitals make this transition metal dichalcogenide more suitable for optoelectronic manipulation. In fact, a necessary ingredient for such valley-contrasting physics is inversion symmetry breaking, which is absent in monolayer and bulk graphene but appears when MoS_2 is formed in a monolayer [4].

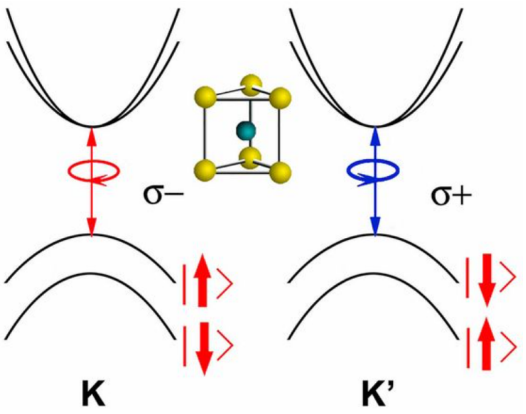

Figure 1. The optical selection rules for valley polarization of electronic states in transition metal dichalcogenides like MoS_2. The relations between spin bands at opposite valleys and the valley-contrasting optical excitation is a result of time reversal symmetry and the spatial inversion symmetry breaking in the monolayer limit of these materials. From [5]

A consequence of these symmetries in the material is that the electrons in each valley will possess their own orbital angular momentum. Because of time reversal symmetry, we expect that the orbital magnetic moments in different valleys will be odd under time reversal, yet spatial inversion symmetry requires that separate valleys have identical magnetic moments [6]. Thus materials with an inversion center, like graphene, will necessarily have zero valley magnetization and are not useful in this context. For MoS_2 monolayers there is no inversion center and the d orbital electrons near the band edge will be opposite for particles in opposite valleys. In particular, the conduction band edge

will be composed of zero-angular momentum d orbital states, whereas the valence band will be made of states with magnetic quantum numbers ± 2 depending on the valley [1]. This will also mean that the valence band splits due to spin-orbit coupling with the relative orientation of spins in each band opposite depending on the valley, as shown in Figure 1. These constraints on the band edge states' angular momenta are directly linked to the absorbed light's helicity that excites electronic states in each valley separately and thus enable optical control of valley polarization.

Kin Fai Mak and colleagues used polarization-tuneable lasers and photodetectors to confirm the theoretical predictions of MoS_2's valley-selective optical excitation in the monolayer limit. They identified two dips in the absorption spectra that correspond to the transition energies between the conduction band edge and the spin-orbit split valence band edges at each valley. These two excitations can be likened to the formation of exciton quasiparticles, which are electron-hole bound pairs formed by such optical excitation. It is immediately clear that the optical selection rules transfer over to the exciton formation rules, and so by looking at the helicity of emitted light after exciton generation we can determine the degree to which each valley is polarized by which kind of circularly polarized light. [3]

This optoelectronic process is performed in Mak et al. (2012), and the resulting polarization-selective data they present is consistent with the results expected by symmetry considerations and conservation of total angular momentum. They were able to exfoliate single and bilayer MoS_2 crystal samples and measure the helicity-resolved photoluminescence spectra for several different laser excitation energies corresponding to the two excitonic resonances and one off-resonance excitation. They observed that at the exciton resonance frequencies and with a specific helicity of circularly polarized light, the emitted spectra from radiative recombination of the excitons was almost entirely made up of photons with the same helicity as the laser used. When researchers used the same optical pumping technique on the bilayer MoS_2 samples, the lack of inversion symmetry breaking meant that the excitations in each valley were equally preferred and so the helicity of the photoluminescence spectrum averaged out to zero. When higher energy off-resonant lasers were used, electrons in both valleys were excited and thus the emission again had zero helicity, confirming that the laser frequency and helicity can be used to selectively populate excitons in each valley independently.

We note that the intensity of emitted light is significantly larger in the monolayer, which again relates to the coupling of valley and spin degrees of freedom. The crystal symmetries in monolayer MoS_2 increase the excitonic lifetimes by virtue of the fact that intervalley scattering is only allowed for atomic-scale scatterers (that provide large momentum change) and simultaneous flipping of the spins to respect the valley-dependent spin-orbit splitting of the valence band [1]. This constraint allows for exciton lifetimes approaching 1 ns and make the monolayer's valley-dependent properties much more pronounced than in the bulk, with a twenty-fold improvement in quantum yield of photoluminescence compared to the bilayer [3].

This result is a stepping stone for many future experiments that manipulate the coupling of spin and valley degrees of freedom in spin-orbit coupled and inversion symmetry breaking materials. Another consequence of the valley asymmetry with regards to spin is that states in each valley experience opposite berry curvatures, which can be observed through the resulting quantum anomalous valley Hall effect when these materials are exposed to electric fields [1]. This leads the way to valley-dependent transport devices and the use of hybrid structures involving valley and spin indices in charge carriers. Additionally, further study of exciton relaxation mechanisms can inform how to construct bound states with longer lifetimes such that imbalance in electronic states between the two valleys can be used for information storage, more precise sensing of polarized light, and other emerging optoelectronic quantum technologies.

References

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