Rydberg series of dark excitons and spin-orbit splitting of the conduction band in WSe₂ monolayer

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Monolayers of transition metal dichalcogenides (TMD) from group VI, such as tungsten diselenide, are recently extensively studied group of semiconducting materials with multi-valley electronic band structure and a direct optical band gap, strong light-matter coupling and existence of robust excitonic complexes. However, despite of decades of intense research on these materials, the knowledge of electronic bands of even the best-studied TMD monolayers remains often quite approximate.

One of the band structure parameters that is not yet known is the amplitude of the spin-orbit coupling (Δ_c) at the edge of their conduction bands. This parameter is of great importance because it influences the interpretation of the basic results of optical and transport experiments, often reported in the study of TMD structures. It has been estimated from various theoretical calculations, but so far has not been derived in an experiment, as being usually only one among other entangled components (e.g., the strength of Coulomb interaction) contributing to the extracted characteristic energies.

Here we derive the amplitude of the spin-orbit coupling in WSe₂ monolayer by comparing the energy ladders of bright (optically active, spin-allowed) and dark (inactive, spin-forbidden) exciton Rydberg series, with the latter appearing in the photoluminescence spectrum only in high in-plane magnetic fields due to the magnetic brightening effect. These bright and dark excitons differ mainly in the band from which the bound electron comes from - the upper or lower subbands of the spin-orbit separated conduction band, respectively. By uncovering the rich Rydberg series of both bright and dark excitonic states, which correspondingly extrapolate to "bright" and "dark" single particle bandgaps, we are able to extract their difference - the amplitude of the spin-orbit coupling $\Delta_c=14$ meV. It is worth noting that this value is much lower than commonly assumed, which calls for revision of theoretical calculations of electronic bands in TMD monolayers.