Understanding the Electronic Structure of Two-Dimensional Perovskites: Quantum and dielectric confinement, and energy Alignment

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Quasi-two-dimensional (2D) perovskites have recently garnered significant attention due to their exceptional optical and electronic properties, making them highly promising candidates for next-generation optoelectronic devices. Their unique structure allows them to retain the advantageous characteristics of both two-dimensional and three-dimensional perovskites while mitigating the inherent challenges associated with extreme thinness in purely 2D systems. One of the defining features of quasi-2D perovskites is the presence of an organic spacer, which plays a crucial role in stabilizing the 2D layered structure. This organic layer introduces both quantum and dielectric confinement effects by energetically forming a quantum well and significantly modifying the permittivity of the material. These effects fundamentally impact charge carrier dynamics, energy level alignment, and overall optoelectronic performance. Therefore, gaining a precise and comprehensive understanding of these confinement effects, along with their implications for band structure modulation, is essential for unlocking the full potential of 2D perovskites in practical applications.

In this study, we systematically investigate how variations in the length and chemical nature of the organic spacer influence both quantum well formation and dielectric confinement effects. A well-structured 2D perovskite serves as an ideal platform for exploring textbook-predicted quantum well behaviors, providing valuable insights into the real-world electronic structure of these materials. By comparing experimental results with theoretical models, we identify key factors that contribute to deviations from expected quantum well phenomena. Understanding these discrepancies is crucial, as they can directly affect charge carrier mobility, exciton binding energy, and interlayer coupling. To achieve a comprehensive characterization, we employ a range of spectroscopic and structural analysis techniques, including Ultraviolet Photoelectron Spectroscopy and Inverse Photoelectron Spectroscopy (UPS-IPES), X-ray Absorption Spectroscopy (XAS), and Wide-Angle X-ray Scattering (WAXS). These advanced experimental methods allow us to probe the electronic states, band alignment, and structural ordering of 2D perovskites with high precision. By correlating these findings, we provide a detailed interpretation of how quantum and dielectric confinement effects influence on the fundamental electronic structure of 2D perovskites.

Based on this understanding, we further explore the energy level alignment in quasi-2D perovskites and how it deviates from conventional theories used to describe heterojunctions. In traditional semiconductor heterostructures, energy alignment is often governed by classical electromagnetism principles, as described by well-established models such as the Z-curve. These models effectively predict band bending and charge transfer at interfaces in semiconductor/semiconductor and metal/semiconductor systems. However, in quasi-2D perovskites, additional complexities arise due to the unique role of the organic spacer layer. Unlike typical inorganic semiconductors, the presence of this organic component introduces an additional spatial and energetic modulation that significantly alters band alignment. In particular, quantum and dielectric confinement effects create deviations from the expected S-curve behavior observed in standard heterojunctions. This deviation has profound implications for charge transport, interfacial recombination, and overall device efficiency. In this presentation, we will analyze these differences in detail, providing both theoretical insights and experimental evidence to elucidate the complex interplay between these factors.

Finally, we extend our discussion to the modulation of the electronic structure of 2D perovskites through doping. Doping strategies are widely employed in traditional semiconductors and three-dimensional (3D) perovskites to tailor their electrical properties, enhance carrier concentration, and improve stability. In 3D perovskites, various doping approaches have been successfully implemented, typically classified based on elemental substitution at the A, B, or X-sites. Additionally, Lewis acid/base molecules have been introduced as A-site (or surface) dopants, leading to significant enhancements in charge transport and device performance. However, in the case of quasi-2D perovskites, successful doping strategies remain relatively underexplored, and the fundamental understanding of doping mechanisms is still limited. This lack of clarity has hindered progress in optimizing the electronic properties of 2D perovskites for practical applications.

To address this knowledge gap, we have systematically investigated different doping methods, each involving distinct energy levels and charge modulation mechanisms. By analyzing the impact of these doping strategies on the electronic structure, we aim to unravel the underlying principles that dictate doping efficacy in 2D perovskites. Our findings highlight key factors that govern dopant incorporation, charge transfer dynamics, and stability within the quasi-2D perovskite framework. These insights provide valuable guidance for future material design, paving the way for more efficient and stable optoelectronic devices based on 2D perovskites. Through this study, we establish a deeper understanding of how to engineer electronic properties in quasi-2D perovskites, ultimately advancing their practical application in light-emitting diodes, photodetectors, and other cutting-edge optoelectronic technologies.