Data-Driven Approach to Understanding Exciton-Exciton Interactions in $CsPbBr_3$ Nanocrystals

By

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Technical Summary:

Lead halide perovskites are a rapidly developing class of materials of interest for optoelectronic applications. They have a number of desirable properties such as long carrier diffusion lengths and defect tolerance that arise from the materials' unique dielectric properties. Although much of the initial interest in lead halide perovskites was geared towards producing highly efficient solar cells from the bulk material, cubic perovskite nanocrystals are a strong candidate system for light-emitting applications. Optical gain in semiconductor nanocrystals relies on emission from biexciton or doubly excited states. Knowledge of the spectral properties of biexciton states is critical for understanding optical gain development as well as many-body interactions between charge carriers more broadly.

In this thesis, we develop and demonstrate a data-driven approach to characterizing the energetics and dynamics of biexciton states in $CsPbBr_3$ nanocrystals using TA spectroscopy. We then use the understanding developed using the TA data to guide experiments using other techniques and further examine the physical phenomena that influence these excited states. We describe our data-driven method in detail and demonstrate its effectiveness in extracting spectral information about $CsPbBr_3$ nanocrystals. The method combines the target analysis fit commonly employed in organic systems with Bayesian inference and a Markov chain Monte Carlo sampler to accurately characterize the model uncertainty and vet the model itself. Applying this analysis to a size-series of $CsPbBr_3$ nanocrystals to allows us to extract the biexciton and exciton component TA spectra as a function of nanocrystal size. We find that the exciton and biexciton spectra have distinctive shapes, in contrast with the common assumption about these spectra. The biexciton spectra a broader and slightly blue-shifted from the exciton spectrum, and the broadening and blue-shifting both increase as the nanocrystal size decreases. This suggests that the exciton-exciton interaction is repulsive rather than binding, but red-shifted optical gain can still be observed from the broader red tail of the biexciton emission spectrum. We verify this with time-resolved photoluminescence experiments.

The central goal of this thesis is to describe a more careful approach to analyzing spectroscopic data. In short, using first-principles to generate a series of assumptions about a complex system can lead to incorrect interpretation of the data. Instead, the data should be first be parsed to separate the information relevant to the experiment using as few assumptions as possible. Once this is done, the data can guide the use of first-principles in the interpretations.

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