Theory of Structural Dynamics and Carrier Mobility in Lead-Halide Perovskites

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Lead-halide perovskites (LHPs) are highly promising materials for solar cells and other optoelectronic devices. Interestingly, the room-temperature magnitude and temperature dependence of a central observable of a semiconductor, the charge carrier mobility, is not fully understood today. At the same time, it is interesting to note that a large amount of complementary experimental and theoretical evidence points to significant anharmonicity in the thermally-activated nuclear motion associated with the lead-halide sublattice of LHPs. These anharmonic nuclear motions are due to a lattice that is soft mechanically, which implies low phonon energies and large nuclear displacements at room temperature. It is currently speculated that these effects may impact the carrier mobility of LHPs. To understand the full range of implications, theoretical models aiming to describe carrier scattering in LHPs clearly need to take the dynamic nuclear fluctuations in these systems fully into account.

Here, I will present our most recent attempts to theoretically describe, explain, and predict the carrier dynamics in LHPs. Our theoretical model takes the dynamic fluctuations in these systems fully into account, by using a multi-scale scheme that is based on density functional theory and molecular dynamics calculations. We use this to approximately compute mobilities of LHPs at different temperatures without any free parameters in the model. Our results show that the impact of anharmonic nuclear fluctuations on the electronic structure can explain the modest mobility of $MAPbI_3$ at room temperature as well as its temperature dependence, in agreement with experimental mobility data. Interestingly, some important effects considered in our model, especially the so-called off-diagonal scattering of electrons and holes, are

typically deemed unimportant for inorganic semiconductors. Here, we find that these are essential for describing the carrier scattering mechanisms in LHPs.

Our findings show that in contrast to high-quality inorganic semiconductors, the carrier transport in LHPs is strongly influenced by anharmonic lattice fluctuations, which cannot be neglected when describing carrier scattering in LHPs. This has an important implication, as it suggests that certain physical observables, including the carrier mobility, cannot be described microscopically within a canonical harmonic phonon picture and the typical scattering models derived from it. Our theory may be applied to predict LHPs with superior charge transport properties, which can serve as a guideline to further improve optoelectronic devices based on these materials.

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