Next Generation Work
Possible future targets at similar or greater rigor include various turbulent flows subjected to other external influences such as buoyancy, solid-body rotation, or electromagnetic forces.

Publications and Data Sets

Lattice Screening and Optical Properties of Novel Perovskite Photovoltaic Materials

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EXECUTIVE SUMMARY
Due to the extremely quick rise of their photocurrent efficiency, hybrid organo-metal-halide perovskites have recently garnered a large amount of attention as potential materials for efficient, cost-effective, and broadly applicable next-generation photovoltaics. However, the influence of excitonic effects on optical absorption and exciton binding energies in these materials is not well understood. In particular, lattice and free-carrier contributions to dielectric screening are currently under investigation. Spin-orbit interaction plays an important role in these materials as well. We use many-body perturbation theory to compute optical properties and an approximate approach to explore the influence of lattice screening. Our results show that when all these effects are taken into account, very good agreement with the experiment is obtained. This work constitutes the first step towards a full, first-principles treatment of these effects that will be broadly applicable for material design of novel photovoltaics.

INTRODUCTION
Hybrid organo-metal-halide perovskites of the form ABX3 have recently garnered a large amount of attention [1]. In this formulation, A is an organic cation, B is a metal cation, and X is the halide anion. Elements such as B={Pb, Sn, Ge} and X={I, Br, Cl} have been investigated, and CH3NH3 is of large interest for A. As a result of their exceptional optical absorption, these materials were used as dye-sensitizers. However, current interest is attributed to the quick rise of photo-conversion efficiencies to more than 20% within a few years. The high photovoltaic efficiency of prototypical CH3NH3PbI3 is important, but also that our approximate first-principles approach to clarify the influence of free-carrier and lattice screening.

They critically determine how efficiently electrons and holes can be separated in a photovoltaic device. Concurrently, a fundamental understanding is needed because excitonic effects and binding energies sensitively depend on the screening of the electron-hole interaction in the material. Better understanding will influence general first-principles models and could lead to an efficient, cost-effective, and broadly applicable set of materials for next-generation photovoltaics.

METHODS & RESULTS
We study optical properties using first-principles, theoretical spectroscopy based many-body perturbation theory [2]. We compute optical absorption spectra by solving a Bethe-Salpeter equation for the optical polarization function. Single-particle energies in the excitonic Hamiltonian are approximated using a generalized-gradient approximation for exchange and correlation. The spin-orbit interaction is approximately included for orbital energies of collinear spins, but not for wave functions used to compute Coulomb matrix elements. Using this approach on Blue Waters, we can accomplish the numerical challenge of converging the optical absorption spectra on Brillouin zone sampling.

The potentially large influence of lattice screening on the electron-hole interaction makes the description of these materials particularly challenging. We employ an approximate technique by Bechstedt et al. to incorporate the influence of lattice polarizability [3]. Experimental work has determined the static dielectric constant to be in the range of 30 to 32 [4], but even values as large as 1,000 were reported [5]. The approximation used here is merely the first step towards a more sophisticated, first-principles approach to clarify the influence of free-carrier and lattice screening.

We compute the optical-absorption spectra of three different polymorphs of CH3NH3PbI3: the low-temperature tetragonal phase used in operational devices (b), and the high-temperature cubic phase (c).

FIGURE 1: Unit cells of the low-temperature tetragonal phase (a), the room-temperature orthorhombic phase (c), and the high-temperature cubic phase (b).

FIGURE 2: Imaginary part of the frequency-dependent complex dielectric function of CH3NH3PbI3 computed using different levels of theory is compared to data from experiment.
treatment of the spin-orbit effect is a reasonable approximation. These results are critically important for development of a comprehensive first-principles approach.

WHY BLUE WATERS

The solution of the Bethe-Salpeter equation is computationally challenging, as it requires computing very large exciton Hamiltonian matrices (ranks more than 100,000). We use either an iterative diagonalization scheme to compute their eigenvalues, or we employ a time-propagation approach to compute optical absorption spectra. Each run requires large amounts of memory, disk storage, and fast communication between the two. Many calculations are needed to ensure convergence of spectra and exciton binding energies on Brillouin zone sampling. Blue Waters provides an outstanding computational package that allows us to carry out these simulations for complicated materials such as CH$_3$NH$_2$PbI$_3$.

Interactions with the Blue Waters team were extraordinarily helpful. As a result, we are now involved in the Joint Laboratory for Extreme Scale Computing (created as part of the Blue Waters Project) aimed at using the efficient ChAISE iterative diagonalization scheme that also runs on graphics processing units (GPUs). While this is work in progress, the Blue Waters project was instrumental in initiating and facilitating this work.

NEXT GENERATION WATER

A next-generation Track-1 system will be instrumental for advanced computational material science research. In our particular field, the most pressing goal is to connect accurate atomistic studies, which fully account for free-carrier screening and electron-phonon effects such as lattice screening, with mesoscale simulations. Furthermore, large-scale materials design requires a large number of such accurate calculations, which, due to their extreme computational cost, can only be achieved on a future Track-1 system. Finally, extending this work towards nanoscale materials such that semiconductor nanocrystals or nanoplatelets will push the computational capabilities of current supercomputers, requires the availability of a future Track-1 system to be successful.

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INTRODUCTION

An improved understanding of fluid-solid heat transfer is crucial for process and component design in multiple engineering applications such as pneumatic conveying systems that transfer powders, granules, and other dry bulk materials through an enclosed pipeline using a combination of pressure differential and the flow of a gas, such as air or nitrogen. The use of computational fluid dynamics (CFD) simulations of multiphase flow are an efficient alternative to experiments for process and design optimization and are becoming more common. Predictive CFD with accurate sub-models has the potential to improve the efficiency of CO$_2$ capture, as well as clean energy generation technologies. The predictive capability of multiphase CFD simulations depends on models for interphase transfer terms such as the closure model for interphase heat exchange.

Although improved gas-solid heat transfer models for CFD simulations have been proposed [1], they are not verified for liquid-solid heat transfer. Extending these improved models to liquid-solid heat transfer requires high-resolution PR-DNS data that capture the flow and thermal features in the boundary layer surrounding individual particles. Since liquids diffuse momentum faster than heat, the thermal boundary layer in liquid-solid flows is thinner than in gas-solid flows. Therefore, in water-solid flow, higher grid resolution is needed to capture the thermal boundary layer accurately. Resources like Blue Waters are needed to simulate the physics accurately. The outcome of physics-based predictive models of liquid-solid heat transfer will result in the better design of pipelines to transport materials safely and efficiently.

METHODS & RESULTS

To simulate heat transfer in liquid-solid flow accurately, PR-DNS using the Particle-resolved Uncontaminated-fluid Reconstructible Immersed Boundary Method (PUREIBM) [2, 3] approach have been performed with high grid resolution. PUREIBM solves mass and momentum equations, and the convective-diffusive scalar transport equation in the liquid phase by imposing exact no-slip and no-penetration boundary conditions on the surface of each isothermal particle. The solid phase is represented using an immersed boundary forcing in the computational domain.

Figure 1(a) shows contours of non-dimensional temperature in steady flow past a fixed homogeneous bed of 644 monodisperse spheres in the cross-sectional plane of a three dimensional periodic cubic box in a dilute flow (solid volume fraction of 0.1). For this simulation of liquid-solid flow with heat transfer, the grid resolution is $D_x = 80$, where $D_x = D_{ax}/D$ is the sphere diameter and $D_{ax}$ is the grid spacing. The flow direction is from left to right. The differences in the shapes of the isotherms between liquid and gas are clearly visible and the benefits of high resolution are also apparent.