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

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LATTICE SCREENING AND OPTICAL PROPERTIES OF NOVEL PEROVSKITE PHOTOVOLTAIC MATERIALS

Allocation: Illinois/500 knh
PI: André Schleife[1]
Co-PI: Joshua A. Leveillee[1]

[1]University of Illinois at Urbana-Champaign

EXECUTIVE SUMMARY

Due to the extremely quick rise of their photoconversion 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 ABX_3 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 CH_3NH_3 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 photo-conversion efficiency of prototypical $CH_3NH_3PbI_3$ needs to be understood to successfully design materials with better performance or improved stability.

For successful device engineering, detailed knowledge of the electronic structure and optical properties is needed. In particular, the influence of excitonic effects on optical absorption and exciton binding energies is not well understood. Exciton binding energies are important because

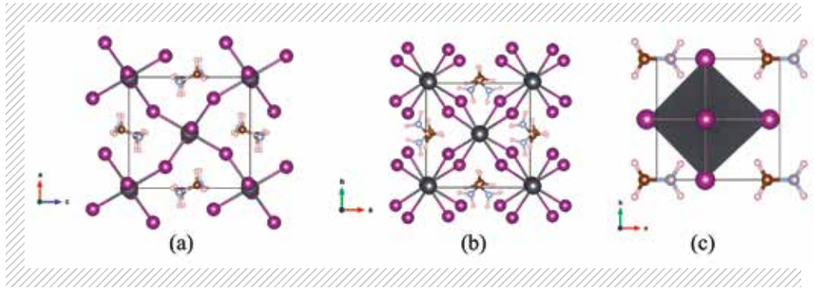

FIGURE 1: Unit cells of the low-temperature orthorhombic phase (a), the room-temperature tetragonal phase used in operational devices (b), and the high-temperature cubic phase (c).

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 $CH_3NH_3PbI_3$: the low-temperature orthorhombic phase, the room-temperature tetragonal phase used in operational devices, and the high-temperature cubic phase (Fig. 1). Our results for the cubic phase in figure 2 indicate a significant influence of the spin-orbit interaction due to heavy lead (Pb) atoms in the material. We also find a significant influence of the lattice screening on the optical-absorption spectra. If the lattice contribution is fully taken into account, excitonic effects are strongly reduced, and the spectrum approaches the density function theory result.

We find very good agreement with an experimental result [6], indicating that not only is lattice screening is important, but also that our approximate

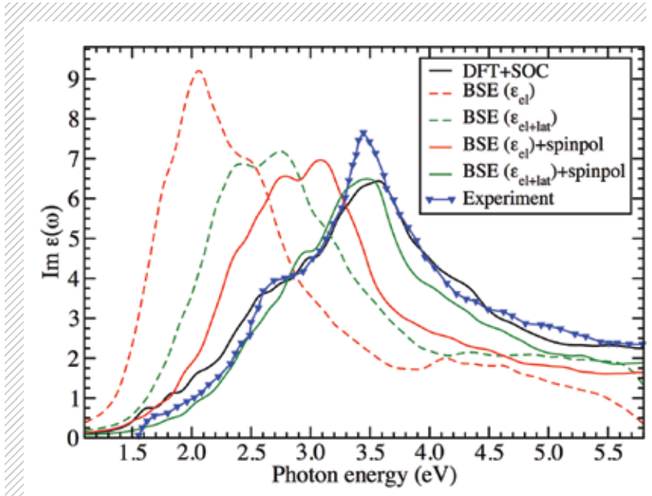

FIGURE 2: Imaginary part of the frequency-dependent complex dielectric function of $CH_3NH_3PbI_3$ computed using different levels of theory is compared to data from experiment.

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 $CH_3NH_3PbI_3$.

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 ChASE 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 WORK

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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PARTICLE-RESOLVED DIRECT NUMERICAL SIMULATIONS OF FLUID-SOLID HEAT TRANSFER

PI: Shankar Subramaniam[1]
Co-PI: Bo Sun[1]

[1]Iowa State University

EXECUTIVE SUMMARY

Heat transfer between solid particles in a fluid flow occur in multiple engineering applications, such as pneumatic conveying. The purpose of this work is to simulate fluid-solid heat transfer using particle-resolved, direct numerical simulation (PR-DNS). Gas-solid heat transfer has previously been simulated and modeled using our PR-DNS approach in a steady flow through a fixed bed of spherical particles. To extend these models to account for liquid-solid heat transfer, such as in a flow of sand particles in water, we need higher resolution simulations to capture the thermal boundary layers surrounding individual particles. Blue Waters enables the study of this heat transfer problem in liquid-solid flow regimes. We simulate heat transfer in steady flow past a fixed bed of spherical particles with high resolution. The PR-DNS database allows us to extend the models for gas-solid heat transfer to liquid-solid heat transfer.

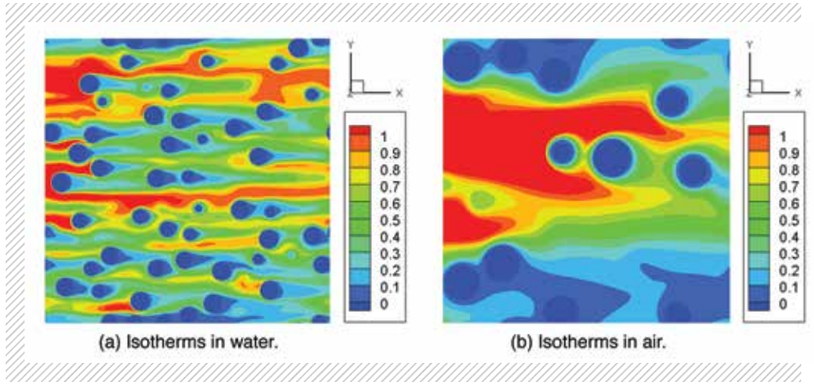

FIGURE 1: A contour plot of the non-dimensional fluid temperature field $\Phi = (T(x,t)-T_s)/(T_{m,in}-T_s)$, where T is the fluid temperature, T_s is the sphere temperature, and $T_{m,in}$ is the bulk fluid temperature, in the cross-sectional plane of a three dimensional periodic computational cubic box at solid volume fraction of 0.1, particle Reynolds number of 20 for (a) Prandtl number of 10 corresponding to water and (b) Prandtl number of 0.7 corresponding to air. The length of the computational cubic box is (a) $15D$ and (b) $7.5D$, where D is the particle diameter. 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.

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 Reconcilable 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 $D_m = 80$, where $D_m = D/\Delta x$, D is the sphere diameter and Δx is the grid spacing. The flow direction is from left to right. It is observed that compared with the gas-solid flow in Figure 1(b), the thinner thermal boundary layer forms around each sphere. A thermal wake behind each particle [4] is also seen for the high Prandtl number of 10. Based on these PR-DNS data, extended models for liquid-solid heat transfer are being developed. The extended models for fluid-solid flow will be used in CFD simulations of industrial applications and enable the designer to optimize the design of industrial systems more accurately and efficiently.