Project Title: Theoretical Spectroscopy for Transparent Conducting Oxides

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Executive summary:
Understanding the influence of dielectric screening on electron-hole interaction and excitonic effects is a long-standing problem in computational materials science. We study dielectric functions of multiple transparent conducting oxides such as In_2O_3, Ga_2O_3, $LaAlO_3$, and HfO_2. These materials are important for applications in the context of transparent electronics and semiconductor industry since they conduct electrical current while being transparent at the same time. The unique combination of high-performance CPUs, large-memory configurations, and a large and fast storage system combined in Blue Waters allows us to gain unprecedented insight into the physics of excitons and the optical properties of these materials. We computed and are computing the most accurate theoretical optical spectra available for these materials and will use our results to further develop the computational framework in order to allow for sustainable computational materials science and highly accurate theoretical spectroscopy for modern, complex materials that drive societal progress.

Description of research activities and results:

Over the last year we investigated transparent conducting oxides, that are wide-band gap semiconductors that are transparent and conducting. They are highly desirable for transparent electronics, photovoltaics, and optoelectronics and their constituent elements are environmentally benign. Because of their properties, oxides such as In_2O_3, Ga_2O_3, $LaAlO_3$, and HfO_2 have been widely adopted as transparent conducting layers and they attract attention as standalone semiconductors in solar-blind photodiodes and Schottky diodes. Despite their appeal and widespread use, especially the influence of the electronic screening on the electron-hole interaction and the optical absorption is poorly understood. This is difficult to measure directly in experiment and theoretical efforts have been hampered by the large unit cell size of In_2O_3 (bixbyite) and β-Ga_2O_3 (monoclinic) with up to 40 atoms, making the use of high-performance computing necessary. Eventually, we aim at understanding the electronic and the ionic contributions to electronic screening – both of which are expected to be important. Current approaches focus almost exclusively on electronic screening of the electron-hole interaction. A deeper understanding is not only important for device applications and semiconductor industry, but it also provides necessary insight for further and ongoing development of the computational framework itself.

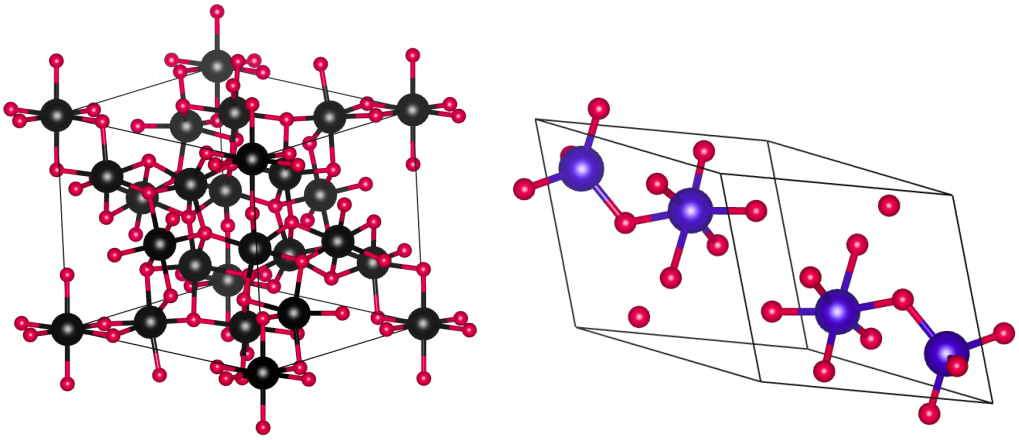

Figure 1: The images show the unit cells of In_2O_3 on the left (In atoms: black, oxygen atoms: red) and Ga_2O_3 on the right (Ga atoms: blue, oxygen atoms: red), as used in the present work.

Our research is based on cutting-edge *first-principles* calculations within many-body perturbation theory: We compute optical absorption spectra using the Bethe-Salpeter equation (BSE) framework based on single-particle energies obtained from a hybrid functional to approximate exchange and correlation. The band gap from a hybrid-functional calculation is reproduced by a semilocal approximation to exchange and correlation and a scissor shift. This approach is suitable to meet the challenging convergence criteria necessary for optical absorption spectra. These techniques allow for predictions of optical properties that are directly comparable to experiment. Insight into optical spectra and the electronic and ionic contributions to dielectric screening are important in order to develop novel optoelectronic materials. Correctly describing these contributions in a first-principles framework is desirable, as it would allow for computational design of optical properties and exciton binding.

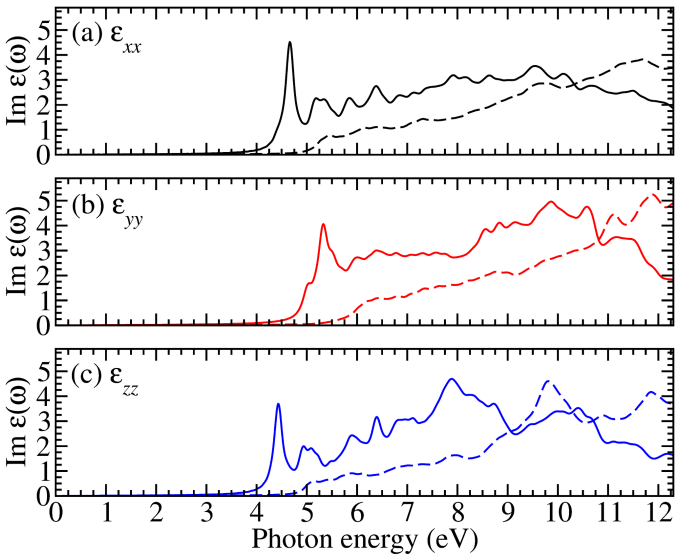

Figure 2: This figure (taken from our publication in Semicond. Sci. Tech.) shows the imaginary part of the anisotropic dielectric function of Ga_2O_3 (solid curves: excitonic and local-field effects are included; dashed curves are computed without those).

For the present research, we computed and analyzed very large exciton Hamiltonian matrices: To study the optical properties of a single material in this work, we computed multiple matrices with ranks between 350k and 378k, leading to memory and storage demands between 0.5 TB and 1 TB for each individual matrix. Computing the matrix is a computationally demanding task itself that we accomplish using a well-parallelized Bethe-Salpeter code. The code uses an ensemble run to divide the work into about 40 to 60 24-hour single-node jobs, each of which is parallelized across all cores of a given node using OpenMP. Once the matrix is written to disk we use a time-propagation approach that scales quadratically with the rank of the matrix to compute an optical absorption spectrum. This code is parallelized using MPI; it reads the matrix and distributes it into the combined memory of 16 Blue Waters nodes in less than five hours (62 MB/sec on average for the duration of 4.7 hours). A time-propagation scheme is then used to compute the optical absorption spectrum in about 6 hours. The scenario described above is not a "one-shot" calculation: Our research requires multiple of these runs for each individual material and, hence, we need a machine such as Blue Waters that allows us to routinely carry out this work for multiple materials and configurations.

Our theoretical-spectroscopy results constitute the most accurate theoretical optical spectra available for these materials. Excitonic effects are explicitly included via the Bethe-Salpeter approach and for the entire spectral range studied here we found a pronounced influence of excitons. The strength of excitonic effects as a function of the photon energy will be explored in a follow-up project where we will extend our results to higher energies to compare with highly accurate experiments up to 40 eV. Our present work also advances the qualitative understanding of optical anisotropy in monoclinic β-Ga_2O_3 both near the absorption edge and at high photon energies. This understanding is necessary for applications of these materials as transparent conducting oxides. From our present and future work in this context we learn how we can model optical properties of technologically

relevant materials (with societally important applications in photovoltaics, transparent electronics, and plasmonics) with very high accuracy by benefitting from efficient parallelization and high-performance computing.

List of publications:

Published:
J. B. Varley and A. Schleife, "Bethe-Salpeter calculation of optical-absorption spectra of In_2O_3 and Ga_2O_3.", Semicond. Sci. Tech. 30, 024010 (2015).

In preparation:
X. Zhang and A. Schleife, "Optical properties of non-equilibrium BN-ZnO."
X. Zhang and A. Schleife, "Theoretical spectroscopy of $LAlO_3$ and HfO_2."

Invited presentations:
5 invited department colloquia in: Binghamton, Chemnitz, Cleveland, Columbia, and Dresden

"First-principles Simulations of Electronic Excitations and Ultrafast Real-time Dynamics in Semiconducting Oxides", Electronic Materials and Applications 2016 (EMA 2016).

Plan for Next Year:

We have already begun to extend this work towards much larger nanoscale systems: Those will require dealing with significantly larger matrices that lead to more demanding requirements for memory, storage, and communication systems. Relaxing the atomic positions of nanoscale systems requires tens to hundreds of nodes on Blue Waters for several days. We are currently limited by the long time it takes the VASP code to write large wave function files and we are working with Blue Waters staff to resolve this issue.

We will also improve our description of electronic screening and aim at a frequency-dependent approach. For this, it will be necessary to update the Bethe-Salpeter Hamiltonian several times. Building on the code that we're currently using, we expect that this can be achieved by using a model function to describe dielectric screening. This will require several runs on several tens of Blue Waters nodes in order to obtain excitonic Hamiltonians. Those matrices require a significant amount of memory per core (see above) in order to efficiently compute optical absorption spectra. We will use numbers of nodes that balance between fast calculations and optimal memory use. In a typical production run we use between 20 and 40 GB of memory per node. We anticipate to use the entire Blue Waters Assistant Professor allocation.

Storage: We are not planning to exceed standard storage quota.
Estimated usage: We anticipate uniformly distributed usage across the year.