

# 2023 INCITE Proposal Submission

## Proposal

**Title:** First-Principles Electron Dynamics in Complex Systems

**Principal Investigator:** Andre Schleife

**Organization:** University of Illinois at Urbana-Champaign

**Date/Time Generated:** 6/17/2022 5:44:38 PM

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## Section 1: PI and Co-PI Information

### Question #1

**Principal Investigator:** The PI is responsible for the project and managing any resources awarded to the project. If your project has multiple investigators, list the PI in this section and add any Co-PIs in the following section.

#### Principal Investigator

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**Question #3**

**Institutional Contact:** For the PI's institution on the proposal, identify the agent who has the authority to review, negotiate, and sign the user agreement on behalf of that institution. The person who can commit an organization may be someone in the contracts or procurement department, legal, or if a university, the department head or Sponsored Research Office or Grants Department.

## Institutional Contact

**Institutional Contact Name**

Robin Beach

**Institutional Contact Phone**

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## Section 2: Project Information

**Question #1**

*Select the category that best describes your project.*

**Research Category**

Materials Science: Condensed Matter and Materials

**Question #2**

*Please provide a project summary in two sentences that can be used to describe the impact of your project to the public (50 words maximum)*

**Project Summary**

We use the Qb@ll and INQ codes on excellent high-performance computing capabilities of ALCF to study complicated exciton dynamics. These processes have significant practical implications for technologically important processes like photocatalysis and hot-electron mediated defect diffusion. Next-generation Ph.D. level researchers will be trained in HPC.

## Section 3: Early Career Track

**Question #1**

## **Early Career**

Starting in the INCITE 2022 year, INCITE is committing 10% of allocatable time to an [Early Career Track](#) in INCITE. The goal of the early career track is to encourage the next generation of high-performance computing researchers. Researchers within 10 years from earning their PhD (after December 31<sup>st</sup> 2012) may choose to apply. Projects will go through the regular INCITE Computational Readiness and Peer Review process, but the INCITE Management Committee will consider meritorious projects in the Early Career Track separately.

**Who Can Apply:** Researchers less than 10 years out from their PhD that need LCF-level capabilities to advance their overall research plan and who have not been a previous INCITE PI.

### **How to Apply:**

In the regular application process, there will be a check-box to self-identify as early career.

- The required CV should make eligibility clear.
- If awarded, how will this allocation fit into your overall research plan for the next 5 years?

Projects will go through the regular INCITE review process. The INCITE Program is targeting at least 10% of allocatable time. When selecting the INCITE Career Track, PIs are not restricted to just competing in that track.

- What is the Early Career Track?
  - The INCITE Program created the Early Career Track to encourage researchers establishing their research careers. INCITE will award at least 10% of allocatable time to meritorious projects.
- Will this increase my chances of receiving an award?
  - Potentially, this could increase chances of an award. Projects must still be deemed scientifically meritorious through the review process INCITE uses each year.
- What do I need to do to be considered on the Early Career Track?
  - In the application process, select 'Yes' at 'If you are within 10 years of your PhD, would you like to be considered in the Early Career Track?' You will need to write a paragraph about how the INCITE proposal fits into your 5-year research and career goals.
- What review criteria will be used for the Early Career Track?
  - The same criteria for computational readiness and scientific merit will be applied to projects in the Early Career Track as will be applied to projects in the traditional track. The different will be manifest in awards decisions by the INCITE management committee.

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## **Early Career Track**

**If you are within 10 years of your PhD, would you like to be considered in the Early Career Track? Choosing this does not reduce your chances of receiving an award.**

No

**If 'yes', what year was your PhD? If 'no' enter N/A**

N/A

**If 'yes', how will this allocation fit into your overall research plan for the next 5 years? If 'no' enter N/A.**

N/A

## **Section 4: INCITE Allocation Request & Other Project Funding/Computing Resources**

### **Question #1**

**OLCF Summit (IBM / AC922) Resource Request - 2023**

### **Question #2**

**OLCF Frontier (Cray Shasta) Resource Request – 2023**

### **Question #3**

**OLCF Frontier (Cray Shasta) Resource Request – 2024**

### **Question #4**

**OLCF Frontier (Cray Shasta) Resource Request – 2025**

### **Question #5**

**ALCF Theta (Cray XC40) Resource Request - 2023**

#### **Node Hours**

1.16 Million Node Hours

**Storage (TB)**

100

**Off-Line Storage (TB)**

50

## Question #6

### **ALCF Polaris Resource Request - 2023**

**Node Hours**

129k Node Hours

**Storage (TB)**

20

**Off-Line Storage (TB)**

10

## Question #7

### **ALCF Polaris Resource Request - 2024**

## Question #8

### **ALCF Polaris Resource Request - 2025**

## Question #9

### **ALCF Aurora (Intel X<sup>e</sup>) Resource Request – 2023**

## Question #10

## **ALCF Aurora (Intel X<sup>e</sup>) Resource Request – 2024**

### **Question #11**

#### **ALCF Aurora (Intel X<sup>e</sup>) Resource Request – 2025**

### **Question #12**

*List any funding this project receives from other funding agencies.*

#### **Funding Sources**

### **Question #13**

*List any other high-performance computing allocations being received in support of this project.*

#### **Other High Performance Computing Resource Allocations**

## **Section 5: Project Narrative and Supplemental Materials**

### **Question #1**

*Using the templates provided here, please follow the [INCITE Proposal Preparation Instructions](#) to prepare your proposal. Elements needed include (1) Project Executive Summary, (2) Project Narrative, (3) Personnel Justification and Management Plan, (4) Milestone Table, (5) Publications Resulting from prior INCITE Awards (if appropriate), and (6) Biographical Sketches for the PI and all co-PI's. Concatenate all materials into a single PDF file. Prior to submission, it is strongly recommended that proposers review their proposals to ensure they comply with the proposal preparation instructions.*

**Concatenate all materials below into a single PDF file.**

- 1. Project Executive Summary (One Page Max)**
- 2. Project Narrative (15 Pages Max)**
- 3. Personnel Justification and Management Plan (1 Page Max)**
- 4. Milestone Table**
- 5. Publications resulting from prior INCITE Awards (if appropriate)**
- 6. Biographical Sketches for the PI and all co-PI's.**

ALCC2022.pdf

The attachment is on the following page.

**Project Executive Summary**

In conversion of solar photons to energy commodities like electricity and fuel, predictive understanding of how excited electrons and electron-hole pairs (excitons) behave in complex matter, such as molecules on surfaces or defects in semiconductors, is central to designing and improving energy conversion processes at the atomistic level. For instance, the dynamics of excitons at the interface of semiconductors and catalytic molecules represents a critical knowledge void that impedes DOE mission critical design of new materials for solar fuel generation, as some of us pursue in the DOE energy innovation hub “CHASE”. Excited electrons near defects in semiconductors increase defect mobility, laying the foundation of the recently emerging field of photo-ionics, with promise of high impact on DOE priorities such as batteries as well as materials design for quantum computing.

Recently, advanced simulations of electronic quantum dynamics in highly complex condensed matter systems with tens of thousands of electrons and femto-second time resolution were enabled by the rapid emergence of high-performance computing and the advancement of massively-parallel real-time TDDFT (RT-TDDFT). The PIs of this proposal, together with collaborators, developed the Qb@ll code over the last years and showed its efficient scalability on more than one million cores. It has enabled us to study electronic excitations in complex systems like DNA in water with more than 13,000 electrons, and oxide semiconductors over hundreds of femtoseconds. In addition to applications, we advanced the code itself by implementing (1) efficient hybrid exchange-correlation functionals using the time-dependent maximally-localized Wannier function technique and (2) TD-current-DFT such that the exchange-correlation vector potential depends on the non-equilibrium time-dependent current. Further computational advancements are increasingly tied to the use of hybrid hardware architectures, including graphics processing units (GPUs). We address this by incorporating the recently developed INQ code into this project, which implements state-of-the-art techniques into a high-performance massively-parallel real-time time-dependent density functional theory (RT-TDDFT) code that efficiently runs on graphical processing units (GPUs).

We propose to use these two new advancements, to reliably study high impact scientific questions associated with dynamics of electrons and ions in complex heterogeneous systems. We will investigate how excitons dissociate at silicon-molecule interfaces, using a hybrid functional to approximate exchange and correlation within RT-TDDFT. Our simulations will uncover the detailed mechanism of how the initial formation of a tightly bound exciton subsequently transitions to a charge transfer exciton across the interface. If successful, this will allow us to understand the materials dependence of the underlying femto- to pico-second time scale of exciton dynamics, allowing for direct comparison to experiment, and facilitating acceleration of this process by materials design and selection. For bulk oxides, such as  $\text{Ga}_2\text{O}_3$  and  $\text{TiO}_2$ , we will use first-principles simulations to provide quantitative predictions for the vacancy migration barrier in the presence of excited electrons due to particle or laser irradiation, as well as the lifetime of excited defect states, and strain dependence. These will guide experimental observation of diffusion enhancement in  $\text{Ga}_2\text{O}_3$  and allow for direct comparison to experimental results on  $\text{TiO}_2$ . We envision that this insight will guide the tuning of radiation parameters (wavelength/intensity for lasers and kinetic energy/charge state for ion projectiles), to exploit the diffusion enhancement for controlling defect distributions in materials of high importance for the semiconductor and quantum computing communities.

In this project we will use the Qb@ll and the INQ code on the excellent high-performance computing capabilities of ALCF. While the parallel performance of Qb@ll for production-level runs has been extensively established for CPU based machines, we will work on similar knowledge within this project for INQ on GPUs. Such type of simulations cannot be performed in university-level computing centers due to the computational cost of cutting-edge first-principles RT-TDDFT simulations applied to non-equilibrium excited-electron dynamics in complex structures. Finally, we note that transferring code from Qb@ll to INQ trains the next generation of Ph.D. level HPC literate scientists. The resulting code will lead to a broadening of the HPC user community, since such novel XC approximations, in combination with a GPU implementation, attract new users to this code and to DOE HPC in general.

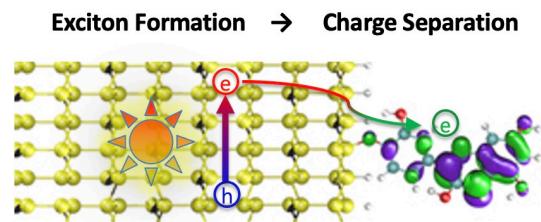
## 1 Significance of Research

Exciton dynamics emerges from femto- to pico-second electron-electron and electron-nuclear interactions that occur after absorption of light or interaction with energetic particle radiation by the electronic system of a material. These complicated relaxation processes turn non-thermalized, non-equilibrium quantum states immediately after the excitation into thermalized electron-hole distributions, critically dominating the underlying time evolution. In addition to tremendous fundamental scientific interest, e.g. in the context of pump-probe spectroscopy experiments, exciton dynamics also has significant practical implications for technologically important processes like photocatalysis, photovoltaics, and hot-electron mediated defect diffusion [1–3]. Progress in exploiting and improving these is currently limited, in particular for extended solids and complex molecular and other low-dimensional systems like surfaces in aqueous solvent, due to a lack of theoretical understanding and insight from quantum-mechanical simulations. We attribute this bottleneck to computational challenges and high cost associated with modern exchange-correlation implementations that are needed to accurately capture the physics of exciton dynamics and the resulting forces on the ions.

Application of such computational techniques to simulate quantum mechanical real-time exciton dynamics is important as it will advance our understanding of non-equilibrium dynamics in complex systems, including exciton dissociation at semiconductor-molecule interfaces and excitation-induced ion mobility in condensed phase systems (see Figs. 1 and 2). This is an urgent need, since the lack of such scientific insight currently impedes materials design that is necessary for key concepts like solar-fuel conversion and photo-ionic systems to become a reality. The simulation techniques tested in this project are free of atom-specific empirical parameters and, hence, are not specific to the particular material systems studied in this project. Thus, in addition to addressing interesting scientific problems for specific materials in this project, we will achieve important broader goals: First, we will gain insights on the broader applicability of these techniques that will directly benefit the large scientific communities of computational materials science and chemistry. Second, we will train the next generation of graduate level researchers in using these simulation techniques on cutting-edge high-performance computers. Finally, we will explore more routine use of GPU enabled simulation software in the context of real-time time-dependent density functional theory, which goes far beyond addressing only a niche problem.

### 1.1 Research Goals

Purposeful, predictive understanding of how electron-hole pairs (excitons) behave in complex matter is central to designing and improving energy conversion mechanisms and devices. For instance, dynamics of excitons at the interface of semiconductors with molecules and water represents a critical knowledge void that impedes design of materials and molecules in solar fuel generation [2, 3]. While time-resolved spectroscopy has advanced greatly in the last twenty years, these experimental techniques require unbiased analysis of spectroscopic signals, often from simulations. At the same time, modeling non-equilibrium dynamics of excitons in complex condensed matter from first-principles remains a significant challenge. In the last decade, great advances were made for modeling of optical absorption spectra using computationally efficient linear-response time-dependent density functional theory (LR-TDDFT). More recently, advanced simulations of electronic quantum dynamics in highly complex condensed matter systems with tens of thousands of electrons and femto-second time resolution were enabled by the rapid emergence of high-performance computing and the advancement of massively-parallel real-time TDDFT (RT-TDDFT). In this context, we advanced the massively parallel Qb@ll code [4, 5], see Sec. 3.2, by implementing (1)



**Figure 1:** A schematic of charge separation at a semiconductor-molecule interface, following optical excitation.

efficient hybrid exchange-correlation functionals using the time-dependent maximally-localized Wannier function technique [6] and (2) TD-current-DFT with an exchange-correlation vector potential that depends on the non-equilibrium time-dependent current [7].

In this project, we aim to explore these implementations in technologically important contexts such as conversion of solar photons to useful energy like electricity and fuel. We will model exciton dynamics at complex semiconductor-molecule interfaces such as those of Si and TiO<sub>2</sub> pursued within the CHASE DOE energy innovation hub. We also model the reduction of vacancy migration barriers in the presence of excited electrons for bulk oxides, such as Ga<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. This will guide experimental observation of diffusion enhancement in technologically important Ga<sub>2</sub>O<sub>3</sub> and will allow for direct comparison to and better understanding of experimental results on TiO<sub>2</sub>.

At the same time, it is the rapid emergence of high-performance computing that enabled us to develop and advance this massively-parallel RT-TDDFT method for simulating quantum dynamics of electrons in highly complex condensed matter systems with tens of thousands of electrons at femto-second resolution. Such an ability to model non-equilibrium exciton dynamics in complex systems is much needed today in various research groups and centers focused on solar energy conversion. However, further computational advancements are increasingly tied to the use of hybrid hardware architectures, including graphics processing units (GPUs). Their routine use in first-principles simulations such as the ones performed in this project needs to be better understood and become more mainstream in the community. We address this by incorporating also the recently developed INQ code into this project, which implements state-of-the-art techniques into a high-performance massively-parallel real-time time-dependent density functional theory (RT-TDDFT) code that efficiently runs on graphical processing units (GPUs) [8].

## 1.2 Impact

We note that this proposed project is in conjunction with the rise of ultrafast spectroscopy and attosecond laser experiments around the world that experimentally probe ultrafast quantum dynamics in many materials. Such experiments motivate our development of an accurate computational description of real-time quantum dynamics through time-dependent quantum-mechanical theory. At the same time, these are complicated and time intensive, rendering a computational description of the underlying physics one of the most desirable goals of computational materials science and chemistry. In addition to advancements in fundamental knowledge, transient quantum states, such as excited electron-hole pairs and their transport, can provide technological breakthroughs for critical and novel applications, including quantum information processing, light harvesting, and neuromorphic computing. We expect this project to have impact in this context.

Furthermore, specific scientific impact of this project lies in the exploration of first-principles techniques that have very high potential to advance knowledge on exciton dynamics in complex systems. Our work will provide numerical results for how exchange and correlation (XC) affects the formation of excitons upon excitation in various materials. We will provide this for a description of XC within TD current-DFT and the long-range correction, as the simplest approach that captures exciton formation, and for hybrid XC functionals that can scale favorably even for large systems with thousands of electrons. Our simulations will advance knowledge on the reliability of these approximations and their computational cost for extended systems of practical relevance, including complex heterogeneous systems like semiconductor-molecule interfaces. At the same time, our results have direct scientific impact, since in all these instances we produce numerical data that will be compared to and guide experiments for the specific materials that we study in this project (see details in Secs. 1.5 and 2.1, and milestone table).

The dynamics of excitons formed at semiconductor-molecule interfaces is one specific area we will impact with this work, particularly for its importance for the CHASE DOE Energy Innovation Hub (see the following section: Relevance to the DOE missions). In particular, formation of charge-transfer excitons and non-linear dynamics of excitons are simulated. The interface between TiO<sub>2</sub> and the catechol molecule has been shown to accommodate interfacial charge transfer excitons, and spectroscopic measurements require

unbiased interpretation based on first-principles simulations. Another key topic we pursue here is how the exciton formed within a semiconductor material like silicon behaves at the interface with molecules. This is particularly an important topic since semiconductor materials are used as solar photon absorber while charge carriers need to transfer to adsorbed catalytic molecules in many solar-fuel generation schemes, including those pursued within CHASE. In the case of diffusion barriers, we will provide quantitative insight into the effect of radiation induced excited states in systems such as  $\text{Ga}_2\text{O}_3$  and  $\text{TiO}_2$ , which will explain the novel photo-ionic effect of excited-electron mediated defect diffusion in these technologically relevant materials. This has potential impact on materials manipulation for the semiconductor industry and for quantum computing.

### 1.3 Relevance to the DOE mission

DOE has spearheaded the nationwide effort on advancing artificial photosynthesis for the production of liquid fuels from sunlight [9]. The initial effort through the Joint Center for Artificial Photosynthesis (JCAP) has been succeeded recently by two newly established DOE hubs, the Liquid Sunlight Alliance (LiSA) and the Center for Hybrid Approaches in Solar Energy to Liquid Fuels (CHASE). Kanai serves as the theory and modeling technique coordinator for the CHASE, overseeing theory efforts for the center. He thus has a firm grasp of center activities, allowing him to directly connect the proposed simulations to experiments in the center. A promising approach pursued by many researchers including those at CHASE is to develop hybrid photoelectrodes for fuel production that combine semiconductors for light absorption together with molecular catalysts for conversion and fuel production. Molecular catalysts are believed to be essential for selective  $\text{CO}_2$  reduction while semiconductors are necessary for optimal absorption of solar photons. Chemical transformation of  $\text{CO}_2$  reduction involves processes like proton-coupled electron transfer by molecular catalysts chemisorbed at the semiconductor surface. Existing codes are unable to simulate such processes because of the lack of necessary capabilities for incorporating exciton dynamics accurately and because simulating such complex structures at an advanced level of theory such as TD-current DFT requires massively-parallel computing on modern GPU-based HPCs such as the ones at DOE's Leadership Computing Facilities.

Our proposed research on defect diffusion will yield quantitative insight into fundamental processes that govern femto-second real-time dynamics of excited electronic states, during and after particle and laser irradiation. Our research will explain the non-adiabatic connection of these excited electronic states to subsequent ion dynamics that follows on longer pico- to nanosecond time scales, and critically determines the evolution from an initial non-equilibrium quantum excited state towards thermalized excited electron-hole distributions. In addition to the specific questions of interest of this project, such insight is necessary to quantitatively understand modern ultrafast pump-probe experiments, including those carried out at DOE's leading experimental facilities such as SLAC. Furthermore, implementing and combining cutting-edge first-principles simulations and applying them to explore their suitability for interesting semiconductors, using massively parallel DOE supercomputers, will benefit the general community of computational condensed matter and materials science researchers. In particular, our work connects to the "out-of-equilibrium and ultrafast response" and the development of "predictive theories and new theoretical methods for the investigation of novel phenomena" goals of TCMP. More broadly, we envision applications of our work that connect to the quantum information goals of DOE BES, such as "Precise Positioning of Atomic Defects", part of PRO1 of the BES Roundtable report on "Opportunities for Basic Research for Next Generation Quantum Systems". We aim to achieve this by guiding precise manipulation of point defects in materials, with the goal of "writing" specific defect concentrations and spatial distributions, e.g. to fabricate materials for single-photon emitter and qubit applications. Exploring the potential for healing materials by removing point defects is our future goal which is in the DOE Condensed Matter and Materials Physics mission space in the context of how "materials respond to external forces such as [...] radiation".

Needs for methodological advancement are clear, in order to overcome these challenges but importantly

also development and testing of code that is capable to take advantage of modern massively parallel and heterogeneous HPC architectures including GPUs. In this project, we will explore the transition from our well-established Qb@ll simulation code to the newly developed INQ code, as a possible answer to this challenge. INQ enhances the capabilities of the earlier Qb@ll code to benefit from GPU-enabled HPC. This is deeply connected to the high-performance computing mission of DOE, as new DOE supercomputers heavily rely on GPUs. Here we will explore modern RT-TDDFT based electronic-structure approaches to model electron-electron interactions within INQ, to enable more widespread use of this code by the community. The simulation techniques developed, implemented, and tested in this project are free of atom-specific empirical parameters and, hence, not specific to the particular material systems studied in this project. Instead of merely addressing a niche problem, they are broadly applicable and will directly benefit the DOE mission across a large scientific community of computational chemistry and materials science. Finally, the resources allocated through this project directly help us addressing the pressing need for training the next generation of Ph.D. level HPC users, which is a demand that is only expected to increase.

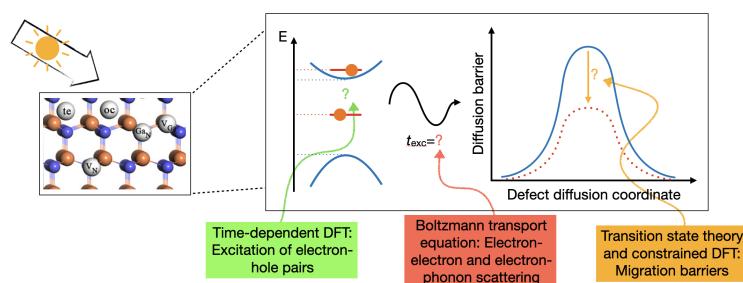
#### 1.4 Relation to Other Projects

The research questions pursued in this project are integrated with the CHASE DOE energy innovation hub on solar fuels. Kanai serves as the theory and simulation technique coordinator for the DOE center, and modeling of exciton dynamics in complex semiconductor systems is fundamental to how solar photons are converted to useful energy commodities. The computational work here is highly synergistic to various efforts pursued in CHASE.

In addition, over the last ten years, Schleife and Kanai have worked closely with the main LLNL development team of the Qb@ll and INQ codes. Both Correa and Andrade visited the Schleife group at UIUC and Schleife sent graduate students from his group to work with the LLNL team at the CCMS summer school. This project will benefit from this close relation between the research groups. The focus of this project is, however, on application of existing code, in particular RT-TDDFT for modeling exciton dynamics and does not collide or compete with any ongoing code or method development work at LLNL, e.g. within the INQ code. Instead, we will feed back any experience from running INQ on Theta-GPU back to the developers at LLNL, to provide practical insight.

#### 1.5 Anticipated Results

We envision two types of results from this project: First, we will obtain specific science outcomes, as we apply novel first-principles computational techniques to simulate quantum mechanical real-time exciton dynamics, advancing our understanding of non-equilibrium dynamics in complex systems such as exciton dissociation at semiconductor-molecule interfaces and excited-electron mediated diffusion of defects in technologically important oxide semiconductors. More specifically, this includes modeling of exciton formation and its dynamics at the interface of semiconductors and molecules, being a key focus area of CHASE, the DOE energy innovation center. Unlike in bulk materials, spectroscopic measurements of excitons at such heterogeneous interfaces are extremely challenging because many spectroscopic techniques are not surface sensitive. In particular, formation of charge-transfer excitons and non-linear dynamics of excitons are simulated using RT-TDDFT. The interface between TiO<sub>2</sub>



**Figure 2: Schematic depiction of physics to be studied and methods used.** Electronic excitations of defects in a semiconductor (GaN) due to particle or laser radiation (left), energy levels and lifetimes  $t_{\text{exc}}$  of defect states (center), and resulting non-adiabatic influence on defect migration barriers (right). Simulation techniques are indicated below.

and the catechol molecule has been shown to accommodate interfacial charge transfer excitons, and spectroscopic measurements require unbiased interpretation based on first-principles simulations. Another key topic we pursue here is how the exciton formed within a semiconductor material like silicon behaves at the interface with molecules. This topic is concerned with how the energy level alignment as well as the surface termination influences exciton dissociation into charge carriers at the interface.

For  $\text{Ga}_2\text{O}_3$  and  $\text{TiO}_2$  we propose original computational research to provide fundamental and quantitative theoretical understanding of increases in defect mobility under electronic excitations that were recently observed both in our own preliminary simulations and in experiments [10]. We aim at an explanation based on the fundamental science of non-equilibrium excited electron configurations, their thermalization, and the emerging influence on non-adiabatic ion mobility. More specifically, we propose to produce quantitative theoretical results for formation energies, energy position and occupation of defect states, their optical excitation energies, excited-state lifetimes, and migration barriers for intrinsic point defects. To this end, we will perform quantum-mechanical first-principles simulations of ground- and excited-state vacancy and interstitial point defects in  $\text{GaN}$ ,  $\text{Ga}_2\text{O}_3$ ,  $\text{TiO}_2$ , or  $\text{SrTiO}_3$  (see Fig. 2). These systems were chosen (i) due to available experimental data ( $\text{TiO}_2$ , see Ref. [10]), which is beneficial for comparison with our simulations, and (ii) high likelihood for success based on theoretical results that hint at low ground-state diffusion barriers [11, 12]. In addition, these materials are currently highly interesting for applications in semiconductor electronics or, potentially, quantum computing. This research is unique since our approach is based on a combination of first-principles techniques, partly developed by our own group [1], that are highly amenable to high-performance computing and use of GPUs, and Boltzmann transport equation simulations, that provide highly precise predictions for a carefully chosen set of defects in semiconductors. The novelty in our approach is that we will use a combination of quantum-mechanical first-principles techniques to directly address the various different time scales involved in excited-electron induced defect migration: In particular, we will use real-time time-dependent density functional theory for describing the dynamics of exciting defects out of the ground state as well as the resulting excited state electron-hole distribution, the Boltzmann transport equation to compute excited-state lifetimes due to electron-electron and electron-phonon scattering, and transition state theory to model migration barriers of defects in their ground and excited state (see Fig. 2). These methods are deemed most appropriate since they accurately describe the excitation dynamics and the physics of electron-electron and electron-phonon interaction underlying this research.

## 2 Research Objectives and Milestones

### 2.1 Goals

#### Exciton Dynamics and Semiconductor-Molecule Interface

**Milestone 1:** The interface between  $\text{TiO}_2$  and the catechol molecule appears to accommodate interfacial charge transfer excitons according to experimental spectroscopic measurements. RT-TDDFT simulations with range-corrected hybrid XC will be performed to simulate the formation of such exotic excitons at this particular interface. We will validate the proposed formation of charge transfer exciton at this interface, which is based on interpretation of spectroscopic measurements. As these approaches to describe XC are not yet implemented in the INQ code, this milestone will be carried out using the Qb@ll code. **Milestone 2:** We will then perform RT-TDDFT to develop molecular-level understanding of exciton dynamics at the interface between silicon and molecules. This topic is concerned with how the energy level alignment as well as the surface termination influences exciton dissociation into charge carriers at the interface. Experimentally, the  $\text{Si}(111)$  surface is terminated with various adsorbant species (e.g. -H, -Cl, - $\text{CH}_3$ ) on purpose and catalytic molecules are chemisorbed on these X- $\text{Si}(111)$  surfaces. We will perform RT-TDDFT simulations of how excitons undergo dissociation into the charge carriers and understand how such quantum-mechanical processes are controlled at the molecular level. As these approaches to describe XC are not yet implemented in the INQ code, this milestone will be carried out using the Qb@ll code. **Success Metrics.** Completion of a simulation of exciton dissociation at a silicon-molecule interface. Observation of initial formation of a

tightly-bound exciton and subsequent transition to a charge transfer exciton across the interface. Comparison of simulated transient absorption spectrum to pump-probe spectroscopy experiments for quantifying the efficiency of exciton dissociation.

### Excited-electron Mediated Defect Diffusion

Our objective is to develop fundamental scientific understanding and quantum-mechanical insight into how ion and laser radiation creates non-equilibrium excited electron-hole states in semiconductors, how these states equilibrate via electron-electron and electron-ion scattering, and how the non-adiabatic character of this process can be exploited for manipulating the defect properties of the host. **Milestone 3:** We will test the central hypothesis that electronic excited states, caused by irradiation, are long lived and significantly reduce the diffusion barrier of point defects in semiconductors, leading to strongly increased diffusivity that can potentially be exploited for precise and targeted manipulation of defect properties (see Fig. 2). For this, we will use the INQ code on GPUs to simulate the excited electronic state of semiconductor defects created by laser irradiation. **Milestone 4:** In addition, we will test the hypothesis that this mechanism shows high defect specificity, due to the characteristic excitation energy fingerprints associated with the defect electronic ground and excited states that contribute to this mechanism. If successful, the proof of concept developed in this project could enable a novel route to manipulate defect properties and atomic geometries in materials with atomic precision. This work is timely as applications include producing single-photon emitters or qubits for quantum computing. Interesting applications would be imminent also for healing damage by triggering high defect mobility in semiconductor devices that are subject to extreme conditions. We will use the INQ code on GPUs to study simultaneous presence of different defects and the selectivity of their excitation as a function of laser frequency. **Success Metrics.** Completion of simulating several femtosecond laser pulses with different energies exciting defect intrinsic point defect states of  $V_{Ga}$  and  $Ga_i$  in  $Ga_2O_3$  and  $V_O$  in  $TiO_2$ . Projection of the resulting time-dependent occupation numbers on ground-state wave functions to determine charge state of the defect after excitation. Comparison of resulting diffusion barriers to experimental observation in  $TiO_2$ .

### Testing and benchmarking of RT-TDDFT simulations on GPUs

While we have successfully used the novel INQ code for electronic stopping RT-TDDFT simulations and also have implemented the time-dependent electric field into the code, we are only now at the stage of using it for production runs, as is discussed in detail in Sec. 3.3. **Milestone 5:** For this reason, we will dedicate one milestone to performing a series of RT-TDDFT simulations on Theta-GPU, to compare to Qb@ll simulations performed in this project and to better understand the performance of INQ across multiple GPUs and, more importantly, across GPUs spread across multiple nodes. For this purpose, we will pick a range of simulation cell sizes and run strong and weak scaling tests. **Success Metrics.** Successful RT-TDDFT simulation on GPUs with INQ, in quantitative agreement with Qb@ll results. Creation of scaling plots and explanation of the observed behavior.

## 2.2 Strategy

Using RT-TDDFT to model dynamics of excitons is a great challenge because of practical approximations employed to describe the electron-electron interaction. In particular, semi-local approximations together with the adiabatic (in time) approximation severely limits the ability of RT-TDDFT to describe excitons. In the context of LR-TDDFT, important progress has been made and a promising approach is the use of screened range-separated hybrid (SRSH) functionals. It was demonstrated that their parameters can be tuned against  $GW$  calculations, making SRSH functionals in TDDFT as accurate as the BSE@ $GW$  method for the calculation of optical absorption spectra for a wide range of semiconductors, including excitonic features. While the BSE@ $GW$  approach remains computationally too expensive for simulating real-time dynamics of systems with thousands of electrons via non-equilibrium Green's function methods, SRSH functionals offer a promising practical approach to exciton dynamics in real systems using RT-TDDFT. In Sec. 2.2.1 we describe our strategy to describe exchange and correlation in this project.

In addition, in order to prepare for the next generation of DOE supercomputers we will also explore time-dependent density functional theory simulations within the modern INQ code [8]. While this code does not yet have all the same capabilities as our Qb@ll implementation, we will perform GPU based RT-TDDFT studies on Theta-GPU within this project, in order to prepare for more extensive use of GPUs in the future. Our strategy for this is briefly outlined in Sec. 2.2.2.

## 2.2.1 Exchange and correlation

Recent important progress reports using hybrid exchange-correlation (XC) functionals within RT-TDDFT [13, 14]. However, when combined with a plane-wave basis, their computational cost is typically about two orders of magnitude higher than that of semi-local functionals [15]. This renders applications to complex extended systems challenging, especially in the context of RT-TDDFT. Here instead we follow up on our recent demonstration of (i) using maximally localized Wannier functions to reduce the computational cost of evaluating exchange integrals [15] and (ii) using a long-range corrected functional along with a vector potential description of exchange and correlation [7]. These two points are described in the following.

**Efficient Hybrid XC with time-dependent Maximally Localized Wannier functions.** We recently demonstrated propagation of maximally-localized Wannier functions (MLWF) in RT-TDDFT [6],

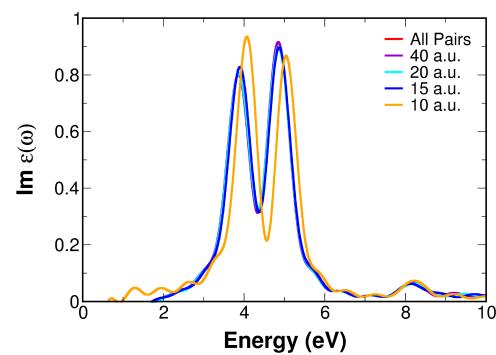
$$i \frac{\partial}{\partial t} w_l(\mathbf{r}, t) = \left[ \widehat{A}^{ML} + \frac{i}{2} \nabla^2 + v(\mathbf{r}) + v'(\mathbf{r}, t) + v_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t) \right] w_l(\mathbf{r}, t), \quad (1)$$

where the maximal localization operator  $\widehat{A}^{ML}$  is an exponential of a unitary matrix that minimizes the spread of the propagating Wannier functions,  $\min \left\{ \sum_n^N \left[ \langle w_n | \widehat{\mathbf{r}}^2 | w_n \rangle - \langle w_n | \widehat{\mathbf{r}} | w_n \rangle^2 \right] \right\}_U$ , and the position operator is given by  $\langle \widehat{\mathbf{r}} \rangle = \frac{L}{2\pi} \text{Im} \ln |\psi| e^{\frac{i2\pi}{L} \widehat{\mathbf{r}}} |\psi\rangle$ . Due to the nearsightedness principle of electrons [16], time-dependent (TD) MLWF orbitals can be made highly localized in space for insulating systems with a finite energy gap. This spatial localization can be exploited for efficiently implementing hybrid exchange-correlation functionals, reducing the computational cost associated with exact exchange integrals [15] in

$$E_x = -\frac{1}{2} \sum_{ij} \iint d\mathbf{r} d\mathbf{r}' \frac{w_i^*(\mathbf{r}, t) w_j(\mathbf{r}, t) w_j^*(\mathbf{r}', t) w_i(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}. \quad (2)$$

The number of exchange integrals that needs to be evaluated can be reduced by recognizing the spatially-localized nature of the TD-MLWFs whereas TD Kohn-Sham wave functions are generally itinerant. Because a minimal spatial overlap is expected for distant TD-MLWFs, one can neglect some of the exchange integrals based on their geometric centers and spreads of the TD-MLWFs in the integrand. Figure 3 shows a preliminary demonstration of the idea using the optical absorption spectrum of crystalline silicon for a small simulation cell. The MLWF center distances are used to determine whether the exchange integrals are calculated between pairs of TD-MLWFs. The optical absorption spectrum remains essentially unchanged even when the cutoff distance is set to the rather small value of only 15 a.u.

Using a representative system of crystalline silicon in a 512-atom simulation cell with 2048 electrons, Fig. 4 shows how the computational cost can be reduced significantly by using this cutoff distance for evaluating the exchange integrals. With



**Figure 3:** Dependence of optical absorption spectrum of silicon calculated using RT-TDDFT with PBE0 via the TD-MLWFs. Only the exchange integrals with TD-MLWF centers closer than the given cutoff (shown from 40 a.u. to 10 a.u.) are included in the calculation.

hybrid XC approximations, the dominant cost of the calculation is the evaluation of the exchange integrals. For this particular case, the computational cost is reduced by an order of magnitude by setting the cutoff distance to a rather large value of 25 a.u. For the calculation of physical properties like an optical absorption spectrum, it is possible to reduce the cutoff distance parameter further as shown in Fig. 3. This approach becomes even more appealing for simulations of increasingly large systems: Thanks to the nearsightedness principle, the acceptable cutoff distance does not scale with system size, and a larger fraction of the exchange integrals can be removed for large systems without degrading accuracy.

In particular, the screened range-separated hybrid (SRSH) [17] approximation is promising as its use in linear response TDDFT successfully describes excitonic features in absorption spectra of real materials that are typically beyond the standard semilocal XC approximation. The SRSH approach thus provides a convenient alternative to the computationally expensive BSE@GW formalism and is expected to enable modeling of exciton dynamics in large complex systems within RT-TDDFT. Another well-known limitation of semi-local XC functionals is their inability to accurately describe long-range charge-transfer excitations. Using SRSH approximations in RT-TDDFT is also expected to greatly facilitate studies of charge-transfer dynamics in heterogeneous systems such as molecule-semiconductor interfaces.

**Long-range Corrected XC Functional.** As discussed above, in most applications of TDDFT local or semi-local approximations were used to describe exchange and correlation to study the dynamics of interacting electrons [14, 18–28], such as the adiabatic local-density approximation (ALDA) or generalized gradient approximations (GGA). However, excitonic effects that are crucial to understand the optical spectra of semiconductors and insulators are not captured by such approximations [29], severely hampering the application of TDDFT in this context and, in particular, in studying their dynamics. Hybrid functionals, such as the ones discussed above, can address this problem in RT-TDDFT [14], but are computationally much more demanding than local or semilocal descriptions of exchange and correlation. To address this, we recently implemented [7] a generalization of the long-range corrected (LRC) kernel used in linear-response TDDFT [30] into the Qb@ll code [4, 5]. We demonstrated that the resulting vector potential accounts for the long-range screened electron-hole interaction and is capable of describing excitonic effects, leading to optical spectra consistent with the linear-response approach. Advantages of this new implementation include computational benefits of RT-TDDFT in the regime of using massively parallel computing and the straightforward treatment of nonlinear effects that are not accessible in the linear response approximation.

We note that this also opens the door to more general developments around real-time TD current-DFT in the future. However, here we initially base our implementation around the simple LRC exchange-correlation kernel [30],  $f_{xc,GG'}^{\text{LRC}} = -\frac{\alpha}{|\mathbf{k}+\mathbf{G}|^2} \delta_{\mathbf{G},\mathbf{G}'}$ , where  $\alpha$  is a functional of the ground-state electron density. Here we treat it as a material-dependent empirical parameter, allowing us to reproduce important features in the optical absorption spectra of insulators and semiconductors and, in particular, strongly bound and continuum excitons. We also set  $f_{xc,GG'}^{\text{LRC}} = 0$  except for  $\mathbf{G} = \mathbf{G}' = 0$ , and we include short-range local-field effects, where  $\mathbf{G}$  and  $\mathbf{G}'$  are non-zero, using the adiabatic local-density approximation (ALDA),  $f_{xc}^{\text{LRC+}} = f_{xc}^{\text{LRC}} + \beta f_{xc}^{\text{ALDA}}$ , see details in Ref. [7]. While other approximations are available [30], the simple expression for  $f_{xc,GG'}^{\text{LRC}}$  captures the  $1/k^2$  behavior that is necessary to describe formation of excitons in three-dimensional solids.

For a real-time implementation of this kernel, the connection to the corresponding TD exchange-correlation

	Cutoff distance (bohr)	Ex integrals evaluated (%)	Energy drift per iteration (a.u.)	Time per iteration (s)	Relative iteration time
PBE	N/A	N/A	$<1.0 \times 10^{-10}$	19.9	0.009
PBE0	N/A	100	$<1.0 \times 10^{-10}$	2227.8	1
PBE0	25	7.4	$4.1 \times 10^{-7}$	271.3	0.12
PBE0	30	9.0	$3.6 \times 10^{-7}$	278.4	0.13

**Figure 4:** Wall-clock time per iteration for a 512-atom (2048 electrons) crystalline silicon simulation cell. This preliminary test was performed on 704 processors (16 Broadwell nodes, Intel Xeon E5-2699A v4 2.4 GHz) using only MPI (no open-MP/SIMD).

potential was established in Ref. [7], using TD current-DFT, where the system evolves according to

$$i \frac{\partial}{\partial t} \varphi_j(\mathbf{r}, t) = \left[ \frac{1}{2} \left( \frac{\nabla}{i} + \mathbf{A}'(\mathbf{r}, t) + \mathbf{A}_{xc}(\mathbf{r}, t) \right)^2 + v(\mathbf{r}) + v'(\mathbf{r}, t) + v_H(\mathbf{r}, t) + v_{xc}(\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t). \quad (3)$$

We then use an exchange-correlation vector potential that is computed from the macroscopic current density,

$$\mathbf{A}_{xc,\mathbf{G}}^{\text{LRC}}(t) = \alpha \int_0^t dt' \int_0^{t'} dt'' \mathbf{j}_{\mathbf{G}}(t'') \delta_{\mathbf{G},\mathbf{z}}. \quad (4)$$

This approach, implemented in the Qb@ll code, has provided reliable results for excitonic spectra of Si, LiF, CsGeCl<sub>3</sub>, and a H<sub>2</sub> chain and in this project we will apply it to study excited-electron dynamics in solids. Based on our Qb@ll implementation we are confident that we will be able to transfer this into the INQ code within this project.

### 2.2.2 Exploring GPU based RT-TDDFT simulations using INQ

The INQ code has been written from scratch, as the need for adapting to GPU-CPU hybrid architectures became clear from the DOE Exascale Computing Initiative and its facilities. INQ offers excellent parallel performance of DFT [8] and RT-TDDFT e.g. on GPUs of DOE supercomputers such as Lawrence Livermore National Lab's Lassen/Sierra, and has been validated against other codes [8]. Currently, Qb@ll is better suited for the science aspects of this project because it has much more functionality than INQ, including the implementation of the descriptions needed for exchange-correlation as outline in Sec. 2.2.1. In addition, Qb@ll is one of only two first-principles codes used in a large-scale fashion for RT-TDDFT simulations of extended materials on leadership scale computers such as NSF's Blue Waters and DOE's Mira or Theta [31, 32]. However, in the future, the new INQ code will assume this role due to its GPU capabilities and it is the most promising entirely US-based contender for RT-TDDFT and non-adiabatic simulations of complex systems. Its implementation is forward-looking in efficiently using exascale GPU-CPU hybrid infrastructures, which is critical for achieving research innovation due to the large computational cost of the above mentioned first-principles techniques, requiring leadership facilities such as Aurora (Argonne) or Frontier (Oak Ridge). This is precisely why we are pushing its use for scientific applications within this project, allowing us to also better understand its limitations, and the technical details that come with the parallel use of GPUs. More specifically, INQ currently only supports Nvidia hardware with the CUDA programming model, i.e. proprietary language extensions and libraries, which poses great challenges for scientists, since these are not supported in the next DOE Leadership Computing Facility's exascale computers. For our work so far we used Theta-GPU, which has NVIDIA A100 hardware. Exploring the current applicability of the INQ code for simulations in this project is beneficial for preparing for porting to the Intel-GPU (Aurora) or AMD GPU (Frontier) in the future, which will also benefit porting to NERSC and NSF machines. In addition, it will provide real-world use cases of the INQ code on GPUs on Theta-GPU.

### 2.3 Dissemination of Results

The results of this project will primarily be disseminated as publications in peer-reviewed scientific journals. The results will also be disseminated in conference presentations, invited talks, and department colloquia both by students using the computational resources and the PIs as appropriate. We have done this very successfully for prior INCITE allocations, resulting in 22 peer-reviewed publications, including in high-impact journals, and more than 20 invited talks or department colloquia.

Newly developed code, if any, will be delivered as part of the official INQ Gitlab repository, following procedures that are already in place [8]. Documentation of the code will be delivered integrated in the code itself, as well as through the Gitlab submission history. Data produced in this project will be stored in the Materials Data Facility (MDF), as we have done before, and will include primary research artifacts (i.e.,

files, directories, raw data, derived data, original codes, etc.) and associated meta-data descriptions to aid future search and discovery, and to improve dataset re-usability.

### 3 Computational Readiness

#### 3.1 Use of Resources Requested

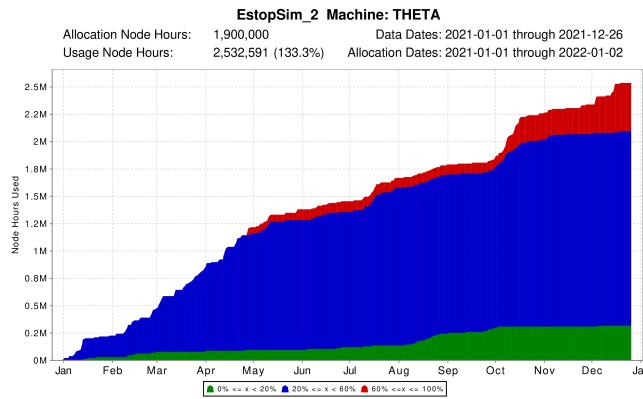
In prior INCITE projects, we have very efficiently run production-scale jobs, in particular on the Theta machine at ALCF (see Fig. 5). The simulations proposed here are very well suited to these types of runs, because (i) they require far more resources than what is typically available in university computing centers or clusters and (ii) they show very favorable parallel scaling, as we discuss below. Since the BlueWaters supercomputer has been terminated, we focus in this project on DOE resources that we have used very efficiently before and, in addition, extend to the GPU heavy Polaris machine, in order to prepare our codes and simulation approaches for the DOE exascale future. The detailed and explicit breakdown of how CPU hours are spread between the milestones and how these numbers are computed are included in the milestone table.

#### 3.2 Computational Approach

##### 3.2.1 Theoretical Formalism and Computational Methods

The possibility of quantitatively describing the non-equilibrium dynamics of electronic and ionic systems in large complex materials under strong external perturbations (e.g. under irradiation of fast ions, electrons, and electromagnetic fields) entirely within first-principles calculations has come within reach. These advances rely on non-perturbative real-time time-dependent density functional theory (RT-TDDFT) [15] and its implementation in efficient electronic-structure codes. Kanai and Schleife jointly developed a large-scale implementation [32, 33] of RT-TDDFT in the plane-wave pseudopotential formalism and successfully applied it to modeling electronic stopping dynamics of light projectile ions such as protons, alpha-particles, and heavy ions in metals, liquids [34], semiconductors, and DNA [35], over a wide range of projectile kinetic energies. We have spent considerable efforts, understanding and resolving technical and theoretical issues such as basis-set effects, channeling vs. off-channeling projectiles, semi-core electron contributions, the time dependence of the projectile charge, and the approximation used to model exchange and correlation, extending existing studies [36] into the high-projectile-velocity regime, including the maximum of electronic stopping power. The theoretical framework of propagating the time-dependent Kohn-Sham equations to perform RT-TDDFT is discussed in more detail in the literature [32] and its specific numerical implementation within Qb@ll in the following section.

Our recent works demonstrated that non-equilibrium simulations based on RT-TDDFT are accurate and well-suited to describe the time-dependent transfer of energy into the electronic system, naturally incorporating non-linear cooperative effects among electronic excitations which are largely missed by models based on linear response theory [36]. While in previous works we focused predominantly on electronic stopping during ion irradiation, in this project, we will shift our attention to the time dependent excitation of the electronic system by light, i.e., a time-dependent electric field [15]. To understand such excitation processes explicitly, we will use the Qb@ll code and a recent implementation of a time-dependent electric field that we achieved together with Xavier Andrade within a previous INCITE project. Our implementation of the large-



**Figure 5:** Previous INCITE utilization data from our team. The detailed and explicit breakdown of how CPU hours are spread between the milestones and how these numbers are computed are included in the milestone table.

scale RT-TDDFT method itself and its usage for studying electronic stopping excitations are summarized in our early publications “Quantum Dynamics Simulation of Electrons in Materials on High-Performance Computers” [32] and more recent progress has been discussed in [15].

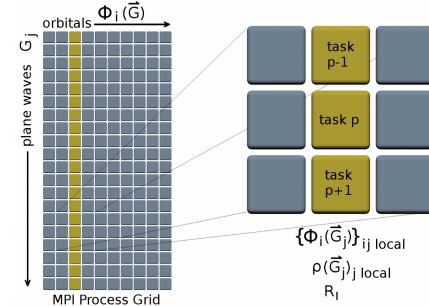
Through multiple years of INCITE support, which unfortunately ended in 2021, our code has been highly optimized for Theta at ALCF. INCITE pushed the technical development of our code to the limit as it had to deal with a highly complex model of DNA solvated in water [15]. The simulation cell consisted of a section of DNA strand with over 10 base pairs and over 1,000 water molecules. This amounts to having more than 13,000 electrons in the simulation cell, and obtaining converged simulations results by propagating more than 6 million plane-wave basis functions. For this large-scale simulation on Theta, we already demonstrated an efficient use of 4,096-node (262,144 cores) jobs, which is 93.3 percent of the entire machine. Recent software development efforts to advance the plane-wave pseudopotential formalism for RT-TDDFT that are worth emphasizing in the context of this proposal include propagation of complex Maximally-localized Wannier functions [6] and dynamical transition orbitals [37]. Such new method developments continue to enable us to gain deeper scientific insights and understanding using highly complex simulations.

### 3.2.2 Description of the Simulation Codes

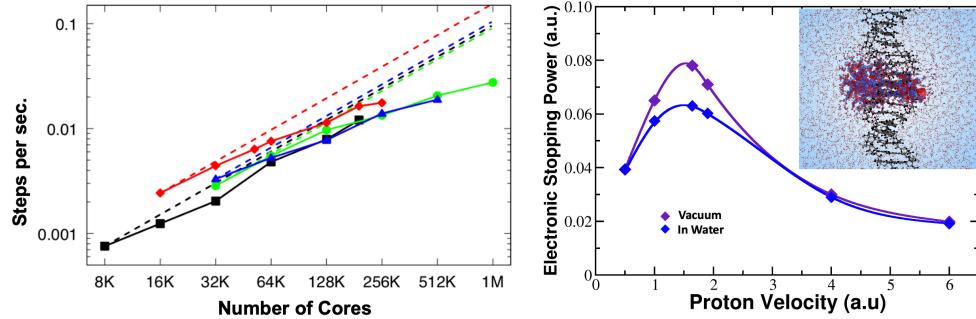
In this project we will use the Qb@ll code [4, 5], that we have successfully used for many scientific applications in the past within the INCITE framework. Here we will use it to perform DFT calculations to obtain fully relaxed electronic ground states as initial condition for subsequent time-dependent simulations. We will then use our massively parallel implementation of RT-TDDFT in Qb@ll to perform production runs of electron and exciton real-time dynamics for various complex materials.

The Qb@ll code is an efficient, scalable implementation of DFT using a plane-wave expansion of the Kohn-Sham (KS) wave functions. Alongside the Octopus code, it is one of only two real-time time-dependent DFT packages that used a plane-wave expansion on up to more than one million compute cores [32]. Written in C++, Qb@ll uses MPI for communication between compute nodes and a mix of OpenMP and threaded kernels to maximize usage of on-node resources (e.g. SIMD parallelism for the AVX-512 on Theta). The Qb@ll code is a branch of the Qbox code developed at Lawrence Livermore National Laboratory (LLNL) by Francois Gygi [4], and was until recently developed mainly by the LLNL group (Erik Draeger/Xavier Andrade), the UNC group (Yosuke Kanai), and the UIUC group (André Schleife). We will use parallel linear algebra as implemented in the ScaLAPACK library and one-dimensional Fourier transforms will be computed with the FFTW or vendor-supplied libraries such as IBM’s ESSL library. For some parts of our RT-TDDFT code operation (e.g. complex matrix operation of time-dependent MLWFs), we implemented our own modification of ScaLAPACK for better efficiency.

The expansion coefficients of the KS electronic wave functions are distributed on a logical 2D process grid, with electronic states distributed across process rows and plane-wave basis functions distributed across process columns (see Fig. 6). The time-dependent (TD) KS equations are well-suited for such a distribution, as nearly all communication can be restricted to sub-communicator collectives within a process row or column. Note that once the ground state of the quantum system is computed (i.e. the initial condition for time-propagation), the TD-KS equation does not require re-orthogonalization of the wave functions or subspace diagonalization at every iteration. Unlike traditional Born-Oppenheimer dynamics, our TD-KS implementation is therefore free of the global communication bottlenecks that could limit strong scalability, as is the case for standard DFT calculations.



**Figure 6:** A schematic illustrating representation of the time-dependent Kohn-Sham electronic wave functions on a two-dimensional logical process grid: Expansion coefficients  $\Phi_i(\vec{G})$  for plane waves (PW) are ordered in terms of the state index  $i$  and the expansion index  $\vec{G}$ .



**Figure 7: Left:** Strong scaling of RT-TDDFT in Qb@ll using the ETRS integrator with LDA XC approximation, over up to 1 million cores. This simulation cell for crystalline gold contains 1,600 atoms (27,200 electrons). Simulations were performed on IBM Blue Gene/Q Sequoia (green) and Mira (blue), Cray XE6 Blue Waters (red), and Cray XC40-Intel KNL Theta (black). **Right:** Demonstration of scientific impact for effects of water solvation on DNA electronic stopping for a particular irradiating proton path through the center of the DNA. This simulation includes more than 13,000 explicit electrons (10 DNA base pairs along the  $z$  direction and over 1000 water molecules).

Currently, this real-time TDDFT implementation uses either an explicit fourth-order Runge-Kutta scheme or the enforced time-reversal symmetry (ETRS) integrator to propagate time-dependent KS equations in real time. Four additional sets of the wave functions are stored in memory for each integration step in the fourth-order Runge-Kutta integration scheme. We constantly make efforts to improve the numerical efficiency of this approach further, by exploring different numerical integration schemes [38]. Analysis of the output will be done using customized scripts that we developed or, e.g. for visualization purposes, we will use third-party tools such as VisIt. Those have been well-tested and used by the team before for similar problems. The same is true for I/O requirements during check-pointing and restarting: A single job typically reads between 10 GB and 600 GB of wave function data in the beginning and writes the same amount of data upon finishing. We will archive this data and expect the total storage needs for all jobs and outputs accumulated to be below 50 TB for the project. While we currently, do not plan to publicly share all of our wavefunction data, we are interested in exploring this option: Schleife currently works closely with Ben Blaiszik, Logan Ward, and ChiMAD, in order to directly connect the ALCF with the Materials Data Facility. This can facilitate sharing data and metadata amongst the team and to publish selected output files along with scientific results. We are in the process of developing a demonstration case of successfully re-using data produced within an INCITE project and published on the Materials Data Facility.

For this project, the broader use of GPUs is the reason that we start shifting away from Qb@ll and towards the new GPU-enabled INQ code [8]. The development of INQ is led by Xavier Andrade and his team at Lawrence Livermore National Laboratory (LLNL), using an open-source Gitlab approach [8] with a strong focus on high adaptability to new hardware. This is indeed a response to growing needs to take advantage of GPU-CPU hybrid computation, which is outside of the Qb@ll code capability we have been developing for the last ten years or so. INQ is implemented as a library, where user input is a computer program, making it very feasible to efficiently implement new developments that interface with the central INQ components [8]. This architecture is very welcoming for community contributions and makes our work sustainable in the future, because improvements to the core code and its inevitable adaptation to future hardware is separated from the implementation of scientific techniques. In this sense, the INQ code is unique, forward-looking, and the developments here are future-oriented, striking an ideal balance between developing new features, while keeping the core of the code adaptable to future technologies and changing hardware requirements.

### 3.3 Parallel Performance

We believe that our RT-TDDFT approach strikes the intricate balance between excellent parallel scaling, that is needed for simulating realistic condensed matter systems, and an accurate first principles description of the

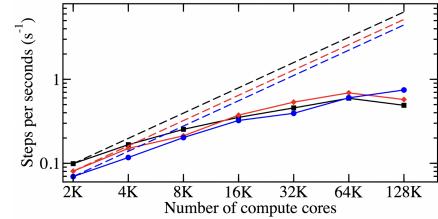
electronic structure and ultrafast electron dynamics. This enables us to exploit massively parallel computing systems to investigate exceptionally interesting scientific questions. Our own implementation [32, 33] of RT-TDDFT in the Qb@ll code, for which efficient scaling up to over 1.5 million cores was demonstrated [31], will be used for the production runs of this project. Similar benchmarks were carried out previously on several different HPC architectures, including Theta, as discussed in Ref. [32] and shown in Fig. 7. The proof of excellent scaling up to more than 1.5 million cores was carried out on the IBM Blue Gene/Q Sequoia machine, which is the largest system (in terms of the number of cores) we had access for testing our code [31]. Using 2,000-atom (22,000 electrons) and 5,400-atom (59,400 electrons) systems, it has achieved up to 58.7 % of the theoretical peak performance on 16,484 cores and 43.5 % on over 1.5 million cores. These fractions of peak performance are excellent results for a first-principles RT-TDDFT study in production-run like scenarios. Using the prior INCITE allocation, we spent significant effort on optimizing our Qb@ll code for Theta. Several PhD students have participated in ALCF Computational Performance workshops over the past several years, working closely with ALCF staff members, Drs. Anouar Benali, William Scullin, and Alvaro Vazquez-Mayagoitia on optimizing the Qb@ll code using the Intel MKL library, working also with local Intel support staff, Michael D'Mello. For the very large case of the solvated DNA, we have demonstrated an efficient usage of Theta by performing several simulations on 4,096-node (262,144 cores), which is  $\approx 93.3\%$  of the entire machine. For illustrating successful adaptation to Theta, Fig. 7 shows strong scaling tests on leadership-class supercomputers, i.e. Sequoia (IBM BG/Q), Blue Waters (Cray XE6/XK7), Mira, (IBM BG/Q), and on Theta (Intel KNL) for a 1,600-atom (27,200 electrons) simulation cell. Note that the performance on Theta is comparable to the performance on Sequoia, the IBM BG/Q machine on which Qb@ll has demonstrated to achieve 50 % of the theoretical peak performance when using 1.5 million cores.

Interestingly, on Theta we observe two different scaling behaviors with a crossover point for more than 32K cores. This is because the larger numbers of cores corresponds to a wider distribution of the calculation across the machine, leading to less memory requirement per node. Thus, the entire calculation fits into (much faster) high-bandwidth memory on Theta for large numbers of cores, leading to a reduction in the wall time needed per simulation time step.

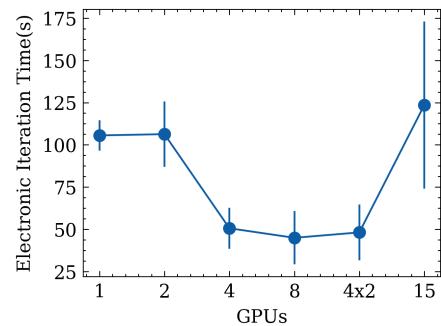
We also tested different MPI/OpenMP strategies on Theta using a 216-atom silicon simulation as an example, see Fig. 8. The three different curves represent different distributions of the simulation between MPI tasks and OpenMP threads. All three curves show that we can scale very well up to 64K cores on Theta, independent of the split between MPI and OpenMP. At the same time, this figure also shows that the exact timings differ slightly. For small numbers of cores up to 16K, it turns out to be optimal to just use MPI tasks to distribute the simulation. However, this data also shows that for larger numbers of cores the distribution between MPI and OpenMP matters: Above 16K nodes, the run with 2 OpenMP threads is fastest and for more than 64K cores, the run where we used 4 OpenMP threads outperforms all other configurations, providing both best timing and best scaling. All this data and our prior experience show that the Qb@ll code is highly optimized on Theta.

**Figure 9:** INQ scaling on Theta-GPU for 64 MgO atoms.

Our expertise with the INQ code is somewhat more limited and will significantly expand with this project.



**Figure 8:** Preliminary results for a 216-atom Si cell on Theta. Black corresponds to MPI only, red uses 2 Open-MP threads, blue uses 4 Open-MP threads.



Our expertise with the INQ code is somewhat more limited and will significantly expand with this project.

Over the last two years the Ph.D. student Yifan Yao has worked closely with Alvaro Vazquez-Mayagoitia at ALCF and Xavier Andrade and Alfredo Correa at LLNL to explore the current feasibility of INQ for the type of simulations proposed in this project. This has convinced us that the simulation capabilities are in place within INQ to carry out electronic-stopping simulations and the time-dependent electric field was transferred from Qb@ll into INQ by Yifan. Hence, we are in an ideal position to (i) carry out the simulations proposed here and (ii) to better understand and improve the parallel scaling behavior of INQ by working with Alvaro, Xavier, and Alfredo. The best scaling plot on GPUs we currently produced is for a  $2 \times 2 \times 2$  MgO simulation cell with 64 atoms (see Fig. 9). This data originates from work with Alvaro and was obtained on Theta-GPU, which has 8 GPUs per node on a total of 32 nodes. We noticed a slight change in timing when multiple nodes but the same total number of GPUs were used, although that change is minor (see 8 vs. "4x2" GPUs in Fig. 9). For larger number of GPUs (15 in Fig. 9) we notice an increase in timing, and need to explain this by (i) improving our statistics and (ii) studying different system sizes (strong scaling). These tests were limited by dominating Kernel launch latency when the studied problem was too small for the number of GPUs used. By understanding this behavior and improving it further, we will gain substantial experience that will benefit the HPC community as new chips become available beyond NVIDIA GPUs. Increasing the number of GPUs was limited partly by very long queue times and we aim to improve over this by using the Polaris machine within this project. The longest timings we have seen for using 2 GPUs on an entire node, in which case a single RT-TDDFT time step took 15 seconds, i.e., 15 node seconds for one time step. In addition, we estimate that increasing the number of atoms to a production size problem increases the cost by a factor of ten. These are the numbers we use to compute the Polaris node estimates.

### 3.4 Developmental Work

The two software packages proposed here, Qb@ll and INQ, are production ready for the simulations proposed here. However, going forward it is desirable to transfer developments we have achieved within Qb@ll over the past years and INCITE projects also into the INQ code. This includes in particular, the long-range corrected kernel and the MLWF implementation discussed above, in order to being able to use the advanced XC approximations also on GPUs. In this project we will work with our own graduate students and with Alvaro at ALCF to explore the extent to which such a transfer can be accomplished without additional funding for graduate student time. Based on our Qb@ll implementation we are confident that we will be able to also implement this into the INQ code within this project. We will also test the performance of any such new implementations within milestone 5 of this project. We note that such work on the code trains the next generation of Ph.D. level HPC literate scientists. The resulting code will lead to a broadening of the HPC user community, since such novel XC approximations, in combination with a GPU implementation, attract new users to this code and to DOE HPC in general.

### 3.5 Data Management Plan

The proposed project is expected to generate digital data in the form of output from electronic-structure codes. The data will be gathered by the research team. The data will be stored in human-readable text or machine-readable binary files: Raw data, graphs, images, videos, etc. generated from this research will be stored in industry-standard digital electronic format (tar, gzip, TIFF, PDF/EPS, AVI, JPG, MOV, PNG, TXT, XLS, DOC). We anticipate the total amount of data generated per year to be on the order of 500 GB.

The project is expected to involve code development and the code will be made available as fully open-source under the Lesser General Public License version 3 (LGPLv3). Code resulting from this work will be available for free download on our web site or on the respective Gitlab pages for INQ. We will use version control systems for source code and post-processing software.

### Data and Metadata Standards

Datasets will be combined with associated metadata descriptions to aid future search and discovery, and to improve dataset reusability. Datasets will be annotated with meta-data according to the Datacite Metadata

Standard (<https://schema.datacite.org>), the Prototype Materials-specific Metadata Schema as provided by NIST and the National Data Service (<http://www.nationaldataservice.org>), and additional meta-data fields will be included as necessary. It is not foreseen that any data collected in pursuit of this program will be sensitive or confidential in nature. We will not dictate the formats of the analyzed data and metadata that must be archived, but suggested formats are discussed next.

### Storage, Retention, Sharing, and Preservation of Access

**Individual storage.** All data and any source code generated from this research will be stored on redundant storage on the PI's server(s). These are backed up daily onto secondary storage that is located in a data center on Campus, geographically removed from the buildings that this research is carried out in. In addition, unlimited Google Cloud storage is available through a Campus agreement.

**Materials Data Facility.** Data set contents stored in the Materials Data Facility (MDF) will include primary research artifacts (i.e., files, directories, raw data, derived data, original codes, etc.) and associated meta-data descriptions to aid future search and discovery, and to improve dataset re-usability.

All data sets associated with publications and certain derived data sets generated by this project will be made available to the public via deposition at the MDF periodically throughout the project (<http://www.materialsdatafacility.org>). Public release should be immediately after publication. Access to and use of the data will be unrestricted and free of charge.

Additional MDF functionality includes services to allow for researchers to 1) deposit large data sets (e.g. many TB); 2) leverage institutional, national, or group storage resources to archive their data sets; 3) associate unique and persistent identifiers; and 4) share their data sets directly with others. MDF also allows the broader community access, retrieve, and download dataset contents via standard HTTP methods or GridFTP for analysis; and find and discover data sets from a centralized location by full text, range, and faceted searches.

**Retention.** The minimum data retention of research data produced in this project is three years after conclusion of the award or three years after public release, whichever is later.

The PI will be responsible for administering and monitoring the short-term storage and backup of the data produced and disseminating certain parts of the data to research participants during the data collection period. Schleife will work with the MDF to ensure long-term storage for all data that is published using the MDF. The PI will be responsible for storing all data that is *not* published using the MDF.

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**Personnel Justification and Management Plan****Personnel Justification**

The entire team is already in place and comprises of two PIs, Yosuke Kanai at UNC and André Schleife at UIUC, as well as students in each of the two research groups. At UIUC, Yifan Yao is a third-year graduate student who is already very experienced in using Qb@ll on Theta and INQ on Theta-GPU from previous INCITE allocations. He will perform all simulations for the Schleife group. At UNC, two PhD students (Chris Shepard and Tom Carney) will perform calculations. They are both experienced with details of the Qb@ll code.

**Management**

Our team of PIs has a long-standing history of working together on similar projects, including a total of five jointly awarded INCITE computer time grants and an NSF-CSSI proposal. We will build on this successful history, continuing our approach that worked well in the past: Each PI will be responsible for the direct mentorship and advising of graduate students and for independent code development in their own group. Joint Zoom meetings every two weeks will be used to discuss progress, mutual overlap, and the scientific direction of the work performed. These meetings are crucial to jointly benefit from developed code and insight from running on Theta and Theta-GPU. They will also help graduate student participants to experience collaborative research and to help each other where appropriate. Any code development will be fed back to the central INQ Gitlab repository. We previously sent multiple students to LLNL to work with the INQ developers during summer schools and will continue to do so in this project, if possible. Schleife will be responsible for the overall coordination of the project and for reporting to the DOE.

**Proposal Title (exactly as it appears on submission): First-Principles Electron Dynamics in Complex Systems**

Lead PI: Schleife

**Year 1**

Milestone:	Details (as appropriate):	Dates:	Status:
<b>1. Charge Transfer Exciton at TiO<sub>2</sub>-catechol molecule</b>	<b>Resource:</b> Theta <b>Node-hours:</b> 0.48 Million <b>Filesystem storage (TB and dates):</b> 100 TB: entire year 2023 <b>Archival storage (TB and dates):</b> 50 TB: entire year 203 <b>Software Application:</b> Qb@ll <b>Tasks:</b> RT-TDDFT simulations with several range-corrected hybrid XC functionals will be performed to simulate the formation of charge transfer exciton at this particular interface. Eight production-level simulations with different XC functionals will be performed with the length of approximately 10 fs for computing the absorption spectrum (8x0.06M/run=0.48M) The node-hour estimate is based on our previous INCITE award. <b>Dependencies:</b> None.	Jan.-Jun., 2023	
<b>2. Dynamics of Exciton Dissociation at Si(111)-molecule interface</b>	<b>Resource:</b> Theta <b>Node-hours:</b> 0.68 Million <b>Filesystem storage (TB and dates):</b> Same as Milestone 1 <b>Archival storage (TB and dates):</b> Same as Milestone 1 <b>Software Application:</b> Qb@ll <b>Tasks:</b> RT-TDDFT simulations with dielectric screened hybrid XC will be performed to simulate exciton dissociation at the particular interfaces. Tentatively, a Ru-based catalytic molecule is planned as the molecular species. 4 production-level simulations with different surface passivation will be performed with the length of approximately 100 fs (4x0.17M/run=0.68M). The node-hour estimate is based on our previous INCITE award. <b>Dependencies:</b> None	Mar.-Dec., 2023	
<b>3. Laser excitation of single semiconductor defects within RT-TDDFT</b>	<b>Resource:</b> Polaris <b>Node-hours:</b> 33 k <b>Filesystem storage (TB and dates):</b> 20 TB: entire year 2023 <b>Archival storage (TB and dates):</b> 10 TB: entire year 203 <b>Software Application:</b> INQ <b>Tasks:</b> 20 RT-TDDFT simulations over 20k time steps, each of which is estimated to require 0.042 node hours per time step based on Theta-GPU timing tests of up to 15 node seconds per time step for 2x2x2 MgO and assuming the larger supercell requires 10 times longer, for Ga <sub>2</sub> O <sub>3</sub> and TiO <sub>2</sub> each with oxygen vacancies under time-dependent electric fields with different frequencies. <b>Dependencies:</b> None.	Jan.-Jun., 2023	
<b>4. Laser excitation of multiple semiconductor defects within RT-TDDFT</b>	<b>Resource:</b> Polaris <b>Node-hours:</b> 66 k <b>Filesystem storage (TB and dates):</b> 20 TB: entire year 2023 <b>Archival storage (TB and dates):</b> 10 TB: entire year 203 <b>Software Application:</b> INQ <b>Tasks:</b> 40 RT-TDDFT simulations over 20k time steps, each of which is estimated to require 0.042 node hours per time step based on Theta-GPU timing tests of up to 15 node seconds per time step for 2x2x2 MgO and assuming the larger supercell requires 10 times longer, for Ga <sub>2</sub> O <sub>3</sub> with oxygen vacancies and gallium	Jul.-Dec., 2023	

Title

Lead PI

	interstitials or vacancies simultaneously present under time-dependent electric fields of different frequency. <b>Dependencies:</b> None.		
<b>5. INQ Benchmarking</b>	<b>Resource:</b> Polaris <b>Node-hours:</b> 30 k <b>Filesystem storage (TB and dates):</b> 20 TB: entire year 2023 <b>Archival storage (TB and dates):</b> 10 TB: entire year 2023 <b>Software Application:</b> INQ <b>Tasks:</b> Ground-state and RT-TDDFT benchmarking for large, complex semiconductor systems and simulation cells using the INQ code. Analyze and possibly improve inter-node parallelism over our Theta-GPU data. The node hour estimate is based on our prior experience with Theta-GPU. <b>Dependencies:</b> None.	Feb.- Aug., 2023	

**Publications resulting from prior INCITE Awards**

- C.-W. Lee and A. Schleife: Hot-Electron-Mediated Ion Diffusion in Semiconductors for Ion-Beam Nanosstructuring. In: *Nano Lett.* **19** (6), pp. 3939–3947 (2019), DOI: [10.1021/acs.nanolett.9b01214](https://doi.org/10.1021/acs.nanolett.9b01214).
- D. C. Yost, Y. Yao, and Y. Kanai: Propagation of maximally localized Wannier functions in real-time TDDFT. In: *J. Chem. Phys.* **150** (19), p. 194113 (2019), DOI: [10.1063/1.5095631](https://doi.org/10.1063/1.5095631).
- C. Shepard, R. Zhou, D. C. Yost, Y. Yao, and Y. Kanai: Simulating electronic excitation and dynamics with real-time propagation approach to TDDFT within plane-wave pseudopotential formulation. In: *J. Chem. Phys.* **155** (10), p. 100901 (2021), DOI: [10.1063/5.0057587](https://doi.org/10.1063/5.0057587).
- Y. Yao, D. C. Yost, and Y. Kanai: *K*-Shell Core-Electron Excitations in Electronic Stopping of Protons in Water from First Principles. In: *Phys. Rev. Lett.* **123**, p. 066401 (2019), DOI: [10.1103/PhysRevLett.123.066401](https://doi.org/10.1103/PhysRevLett.123.066401).
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- H. Vázquez, A. Kononov, A. Kyritsakis, N. Medvedev, A. Schleife, and F. Djurabekova: Electron cascades and secondary electron emission in graphene under energetic ion irradiation. In: *Phys. Rev. B* **103**, p. 224306 (2021), DOI: [10.1103/PhysRevB.103.224306](https://doi.org/10.1103/PhysRevB.103.224306).
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- A. Kononov and A. Schleife: Pre-equilibrium stopping and charge capture in proton-irradiated aluminum sheets. In: *Phys. Rev. B* **102**, p. 165401 (2020), DOI: [10.1103/PhysRevB.102.165401](https://doi.org/10.1103/PhysRevB.102.165401).
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- C.-W. Lee and A. Schleife: Electronic stopping and proton dynamics in InP, GaP, and  $In_{0.5}Ga_{0.5}P$  from first principles. In: *Eur. Phys. J. B* **91** (10), p. 222 (2018), DOI: [10.1140/epjb/e2018-90204-8](https://doi.org/10.1140/epjb/e2018-90204-8).
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- K. G. Reeves and Y. Kanai: Electronic excitation dynamics in liquid water under proton irradiation. In: *Sci. Rep.* **7**, pp. 1–8 (2017), DOI: [10.1038/srep40379](https://doi.org/10.1038/srep40379).
- K. G. Reeves, Y. Yao, and Y. Kanai: Electronic stopping power in liquid water for protons and  $\alpha$  particles from first principles. In: *Phys. Rev. B* **94**, p. 041108 (2016), DOI: [10.1103/PhysRevB.94.041108](https://doi.org/10.1103/PhysRevB.94.041108).
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**Curriculum Vitae**  
**André Schleife, Associate Professor**

Department of Materials Science and Engineering, U. of Illinois, 1304 W. Green St., Urbana, IL 61801  
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### Professional Preparation

Friedrich-Schiller Univ. Jena, Germany	Physics	Dr. rer. nat. (Ph.D.)	2010
Friedrich-Schiller Univ. Jena, Germany	Physics	Diploma (M.S.)	2006
Technical Univ. Chemnitz, Germany	Physics	Vordiplom	2003

### Appointments

2020-present	Blue Waters Associate Professor, Department of Materials Science and Engineering, University of Illinois, Urbana, IL
2013-2020	Blue Waters Assistant Professor, Department of Materials Science and Engineering, University of Illinois, Urbana, IL
2011-2013	Directorate Postdoctoral Researcher, “Quantum Simulations Group”, Lawrence Livermore National Laboratory, Livermore, CA
2010-2011	Postdoctoral Researcher, “Condensed Matter Theory Group”, Friedrich-Schiller-University, Jena, Germany

### Five Publications Most Relevant to This Proposal

1. C.-W. Lee, J. A. Stewart, R. Dingreville, S. M. Foiles, **A. Schleife**, “Multiscale simulations of electron and ion dynamics in self-irradiated silicon” Phys. Rev. B 102, 024107 (2020).
2. A. Kononov, **A. Schleife** “Pre-equilibrium stopping and charge capture in proton-irradiated aluminum sheets” Phys. Rev. B 102, 165401 (2020).
3. C.-W. Lee, **A. Schleife** “Hot-Electron-Mediated Ion Diffusion in Semiconductors for Ion-Beam Nanostructuring” Nano Lett. (2019).
4. C.-W. Lee, **A. Schleife** “Electronic stopping and proton dynamics in InP, GaP, and In<sub>0.5</sub>Ga<sub>0.5</sub>P from first principles” Eur. Phys. J. B 91, 222 (2018).
5. E. W. Draeger, X. Andrade, J. A. Gunnels, A. Bhatele, **A. Schleife**, and A. A. Correa. “Massively parallel first-principles simulation of electron dynamics in materials,” J. Parallel Distr. Comp. **106**, 205–214 (2017) (Best Paper, Applications)

### Research Interests and Expertise

My group uses advanced computation to understand and predict this intricate interplay for materials in electronic and energy applications and under extreme conditions. We study electronic excitations, triggered by interaction with electromagnetic and particle radiation, and subsequent femto-second relaxation processes. We have extensive expertise with first-principles simulations, based on density functional, many-body perturbation, and time-dependent density functional theory, of hard materials, modern semiconductors, and nanomaterials. We also aim to implement numerical and methodological improvements into first-principles codes.

### Synergistic Activities:

**Awards:** Office of Naval Research Young Investigator Award (2018); National Center for Supercomputing Applications Fellowship (2017); NSF CAREER Award (2016); Physical and Life Sciences Directorate Outstanding Postdoc Award (2012); Heptagon “Sven-Bühling” prize (2007)

**Outreach:** High-school student outreach within “Upward Bound” (since 2015); Contributor to “Girls Learning About Materials” Summer Camp (since 2015)

**Community development:** Editorial Board member “Electronic Structure” and “Journal of Physics: Condensed Matter”; Co-organizer of Focus Topics, Tutorials, and Invited Symposia at APS March

Meeting (2015–2020); Co-organizer of summer school and workshop on TDDFT (Telluride, 2017 and 2019); Co-organizer of a Mini Symposium on “Large Scale Electronic-Structure Calculations on Modern and Future High-Performance Supercomputers”, Platform for Advanced Scientific Computing (PASC) Conference, Basel, Switzerland;

**Collaborators and Co-Editors in last 60 months (exlc. UIUC collaborators due to page limit).**

S. Achilles (Forschungszentrum Juelich), M. Aeschlimann (U of Kaiserslautern), X. Andrade (Lawrence Livermore National Laboratory), J. Andreasson (ELI Beamlines, Czech Republic), A. Baczeski (Sandia National Lab), H. Bale (Carl Zeiss, Pleasanton), M. Bernardi (Caltech), S. Bevilacqua (Caltech), J. Boland (U of Manchester), S. Bone (SLAC), A. Boubnov (Karlsruhe Institute of Technology), M. Burdanova (U of Warwick), S. Carney (The Institute of Optics, U of Rochester), T. Cocker (Michigan State U), E. Constantinescu (Argonne National Lab), A. Correa (Lawrence Livermore National Laboratory), F. da Jornada (Stanford U), K. Dani (Okinawa Institute of Science and Technology Graduate U), P. Darancet (Argonne National Lab), C. Deparis (U Cote d'Azur), E. Di Napoli (Forschungszentrum Juelich), R. Dingreville (Sandia National Lab), F. Djurabekova (U of Helsinki), S. Espinoza (ELI Beamlines, Czech Republic), N. Esser (Leibniz-Institut für Analytische Wissenschaften), J. Even (Univ Rennes), M. Feneberg (Otto-von-Guericke-Universität Magdeburg), A. Ferguson (U of Chicago), S. Filippone (Massachusetts Institute of Technology), S. Foiles (Sandia National Lab), M. Frontzek (SLAC), Z. Galazka (Leibniz-Institut für Kristallzüchtung), M. Gatti (École Polytechnique, Institut Polytechnique de Paris), R. Goldhahn (Otto-von-Guericke-Universität Magdeburg), V. Gorelov (École Polytechnique, Institut Polytechnique de Paris), A. Gottwald (Physikalisch-Technische Bundesanstalt), M. Grundmann (U of Leipzig), R. Haas (National Center for Supercomputing Applications), S. Hansen (Sandia National Lab), K. Hattar (Sandia National Lab), F. Hegmann (U of Alberta, Canada), O. Herrfurth (U of Leipzig), R. Jaramillo (Massachusetts Institute of Technology), D. Johnson (U of Oregon), B. Jones (IBM, Almaden), L. Ju (Massachusetts Institute of Technology), Y. Kanai (U of North Carolina, Chapel Hill), K. Kang (Fritz-Haber Institute Berlin, Germany), H. Kapteyn (U of Colorado and NIST, Boulder, CO), C. Katan (Univ Rennes), H. Katz (Johns Hopkins U), R. Kukreja (U of California, Davis), M. Kloz (ELI Beamlines, Czech Republic), N. Koocher (Northwestern U), R. Kukreja (U of California, Davis), A. Kyritsakis (U of Helsinki), C. Lee (Colorado School of Mines), J. Leveille (U of Texas, San Antonio), I. Lu (Caltech), W. Lambrecht (Case Western Reserve U), J. Lloyd-Hughes (U of Warwick), A. Martinolich (Caltech), N. Medvedev (Academy of Science of Czech Republic), S. Meng (Chinese Academy of Sciences, Beijing), R. Milot (U of Warwick), G. Mitchson (U of Oregon), N. Modine (Sandia National Lab), A. Mohite (U of Houston), M. Murnane (U of Colorado and NIST, Boulder, CO), J. Neufeind (Oak Ridge National Lab), A. Neukirch (Los Alamos National Lab), M. Neumann (Leibniz-Institut für Analytische Wissenschaften), S. Niu (U of Southern California), J. Nixdorf (Otto-von-Guericke-Universität Magdeburg), V. Novosad (Argonne National Lab), A. Olmstead (Sandia National Lab), P. Oppeneer (Uppsala U), M. Preefer (UCSB), E. Prinz (U of Kaiserslautern), I. Radu (Freie Universität Berlin), J. Ravichandran (U of Southern California), M. Rebarz (ELI Beamlines, Czech Republic), L. Reining (École Polytechnique, Institut Polytechnique de Paris), S. Richter (U of Leipzig), A. Robinson (George Mason U), J. Rondonelli (Northwestern U), A. Rubio (Max Planck Institute for the Structure and Dynamics of Matter, Hamburg), M. Ruggenthaler (Max Planck Institute for the Structure and Dynamics of Matter, Hamburg), R. Schmidt-Grund (U Ilmenau), J. Schuster (TU Chemnitz), K. See (Caltech), M. Sentef (Max Planck Institute for the Structure and Dynamics of Matter, Hamburg), E. Shapera (U of Graz, Austria), X. Shi (U of Colorado and NIST, Boulder, CO), K. Shmilovich (U of Chicago), J. Sklenar (Wayne State U), B. Stadtmüller (U of Kaiserslautern), J. Stewart (Sandia National Lab), J. Sun (Max Planck Institute for the Structure and Dynamics of Matter, Hamburg), Y. Takamura (U of California, Davis), J. Tovar (Johns Hopkins U), S. Tretiak (Los Alamos National Lab), C. Ullrich (U of Missouri), H. Vazquez (U of Helsinki), P. Vora (George Mason U), C. Wagner (TU Chemnitz), J. Winkelmann (Forschungszentrum Juelich), Y. Yao (U of North Carolina, Chapel Hill), K. Ye (Massachusetts Institute of Technology), M. Yeung (Massachusetts Institute of Technology), X. Zhang (U of Michigan), B. Zhao (U of Southern California), L. Zhou (Los Alamos National Lab), S. Zollner (New Mexico State U), J. Zuniga-Perez (U Cote d'Azur), F. Bechstedt (Friedrich Schiller U Jena, Germany), R. Niemininen (Aalto U), G. Pacchioni (Università degli Studi di Milano-Bicocca, Italy)

**Curriculum Vitae (2-page limit)**  
Yosuke Kanai  
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University of North Carolina at Chapel Hill  
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Phone : (919) 962-2891

### Professional Preparation

- 2006:** Princeton University; Ph.D. in Theoretical Chemistry  
**2003:** Princeton University; M.A. in Theoretical Chemistry  
**2001:** University of Tennessee, B.S. (Honors) in Chemistry

### Appointments

- 2022-current:** Professor, Department of Chemistry, University of North Carolina at Chapel Hill  
**2017-2022:** Associate Professor, Department of Chemistry, University of North Carolina at Chapel Hill  
**2011-2017:** Assistant Professor, Department of Chemistry, University of North Carolina at Chapel Hill  
**2011-2014:** Visiting Scientist, Condensed Matter and Materials Division, Lawrence Livermore National Laboratory  
**2009-2011:** Lawrence Fellow, Condensed Matter and Materials Division, Lawrence Livermore National Laboratory  
**2006-2009:** BNNI Post-doctoral Scholar, University of California at Berkeley

### Five Publications Most Relevant to This Proposal

- (1) "Dynamical Transition Orbitals: A Particle-Hole Description in Real-time TDDFT Dynamics" R. Zhou and Y. Kanai, **J. Chem. Phys.**, 154, 054107 (2021)
- (2) "First-Principles Demonstration of Nonadiabatic Thouless Pumping of Electrons in a Molecular System" R. Zhou, D. C. Yost, Y. Kanai, **J. Phys. Chem. Lett.**, 12, 4496 (2021).
- (3) "Simulating Electronic Excitation and Dynamics with Real-time Propagation Approach to TDDFT within Plane-wave Pseudopotential Formulation" C. Shepard, R. Zhou, D. C. Yost, Y. Yao, Y. Kanai, **J. Chem. Phys.**, 155, 100901 (2021)
- (4) "K-shell Core Electronic Excitation in Electronic Stopping of Protons in Water from First Principles" Y. Yao, D. C. Yost, Y. Kanai, **Phys. Rev. Lett.**, 123, 066401 (2019).
- (5) "Propagation of Maximally Localized Wannier Functions in Real-Time TDDFT" D. Yost, Y. Yao, Y. Kanai, **J. Chem. Phys.**, 150, 194113 (2019)

**Research Interests and Expertise**

Development and application of large-scale first-principles electronic structure methods in combination with other computational methods such as molecular dynamics and quantum dynamics simulations to understand novel dynamical phenomena in extended systems.

**Synergistic Activities**

- Editorial Advisory Board member, Journal of Physical Chemistry Letters, 2019-
- Graduate Faculty member, Dept. of Chemistry, Duke University, 2016-
- Organizer, HybriD3 Theory Training Workshop, Duke University, 1/28-29/2021
- Organizer, "High-Performance Computing and Electronic Structure Calculations in Materials Research" Japan Society of Applied Physics-Materials Research Society Joint Symposia, Kyoto, Japan, 9/16-20/2013.
- Organizing Committee member for Solar Energy + Technology, Conference Chair, "Solar Hydrogen and Nanotechnology VIII" Optics + Photonics SPIE Meeting, San Diego, CA, 8/25-29/2013.
- Member, Theory Facility Proposal Study Panel, Molecular Foundry, LBNL, 2011-2014
- Director, Computational Chemistry and Materials Science Summer Institute, LLNL, 2009-2011

**Collaborators (*past 5 years including name and current institution*)**

Heiko Appel (Max Planck Institute, Germany), Victor Batista (Yale University), Max Berkowitz (University of North Carolina Chapel Hill), Volker Blum (Duke University), James Cahoon (University of North Carolina at Chapel Hill), Alfredo Correa (Lawrence Livermore National Laboratory), Erik Draeger (Lawrence Livermore National Laboratory), Peter Kratzer (Univ. of Duisburg-Essen, Germany), Tim Lian (Emory), Andrew Moran (University of North Carolina at Chapel Hill), Thomas Meyer (University of North Carolina at Chapel Hill), Sharon Hammes-Schiffer (Yale University), Andre Schleife (University of Illinois at Urbana Champaign), Xinguo Ren (University of Science and Technology of China, PR-China), Patrick Rinke(Aalto University, Finland), Wei You (University of North Carolina at Chapel Hill)

## Section 6: Software Applications and Packages

### Question #1

Please list any software packages used by the project, and indicate if they are on open source or export controlled.

#### Application Packages

##### Package Name

Qb@ll

##### Indicate whether Open Source or Export Controlled.

Open Source

##### Package Name

INQ

##### Indicate whether Open Source or Export Controlled.

Open Source

## Section 7: Wrap-Up Questions

### Question #1

National Security Decision Directive (NSDD) 189 defines Fundamental Research as "basic and applied research in science and engineering, the results of which ordinarily are published and shared broadly within the scientific community, as distinguished from proprietary research and from industrial development, design, production, and product utilization, the results of which ordinarily are restricted for proprietary or national security reasons." Publicly Available Information is defined as information obtainable free of charge (other than minor shipping or copying fees) and without restriction, which is available via the internet, journal publications, textbooks, articles, newspapers, magazines, etc.

The INCITE program distinguishes between the generation of proprietary information (deemed a proprietary project) and the use of proprietary information as input. In the latter, the project may be considered as Fundamental Research or nonproprietary under the terms of the nonproprietary user agreement. Proprietary information, including computer codes and data, brought into the LCF for use by the project - but not for generation of new intellectual property, etc., using the facility resources - may be protected under a nonproprietary user agreement.

## Proprietary Information

**Are the proposed project and its intended outcome considered Fundamental Research or Publicly Available Information?**

Yes

**Will the proposed project use proprietary information, intellectual property, or licensing?**

No

**Will the proposed project generate proprietary information, intellectual property, or licensing as the result of the work being proposed?**

*If the response is Yes, please contact the INCITE manager, [INCITE@doeleadershipcomputing.org](mailto:INCITE@doeleadershipcomputing.org), prior to submittal to discuss the INCITE policy on proprietary work.*

No

## Question #2

*The following questions are provided to determine whether research associated with an INCITE proposal may be export controlled. Responding to these questions can facilitate - but not substitute for - any export control review required for this proposal.*

*PIs are responsible for knowing whether their project uses or generates sensitive or restricted information. Department of Energy systems contain only data related to scientific research and do not contain personally identifiable information. Therefore, you should answer "Yes" if your project uses or generates data that fall under the Privacy Act of 1974 U.S.C. 552a. Use of high-performance computing resources to store, manipulate, or remotely access any national security information is prohibited. This includes, but is not limited to, classified information, unclassified controlled nuclear information (UCNI); naval nuclear propulsion information (NNPI); and the design or development of nuclear, biological, or chemical weapons or of any weapons of mass destruction. For more information contact the Office of Domestic and International Energy Policy, Department of Energy, Washington DC 20585, 202-586-9211.*

## Export Control

**Does this project use or generate sensitive or restricted information?**

No

**Does the proposed project involve any of the following areas?**

- i. Military, space craft, satellites, missiles, and associated hardware, software or technical data**
- ii. Nuclear reactors and components, nuclear material enrichment equipment, components (Trigger List) and associated hardware, software or technical data**
- iii. Encryption above 128 bit software (source and object code)**
- iv. Weapons of mass destruction or their precursors (nuclear, chemical and biological)**

No

**Does the proposed project involve International Traffic in Arms Regulations (ITAR)?**

No

### **Question #3**

*The following questions deal with health data. PIs are responsible for knowing if their project uses any health data and if that data is protected. Note that certain health data may fall both within these questions as well as be considered sensitive as per question #2. Questions regarding these answers to these questions should be directed to the centers or program manager prior to submission.*

#### **Health Data**

**Will this project use health data?**

No

**Will this project use human health data?**

No

**Will this project use Protected Health Information (PHI)?**

No

### **Question #4**

*The PI and designated Project Manager agree to the following:*

#### **Monitor Agreement**

**I certify that the information provided herein contains no proprietary or export control material and is correct to the best of my knowledge.**

Yes

**I agree to provide periodic updates of research accomplishments and to acknowledge INCITE and the LCF in publications resulting from an INCITE award.**

Yes

**I agree to monitor the usage associated with an INCITE award to ensure that usage is only for the project being described herein and that all U. S. Export Controls are complied with.**

Yes

**I understand that the INCITE program reserves the right to periodically redistribute allocations from underutilized projects.**

Yes

## **Section 8: Outreach and Suggested Reviewers**

### **Question #1**

*By what sources (colleagues, web sites, email notices, other) have you heard about the INCITE program? This information will help refine our outreach efforts.*

#### **Outreach**

**By what sources (colleagues, web sites, email notices, other) have you heard about the INCITE program? This information will help refine our outreach efforts.**

Previous INCITE awards

### **Question #2**

#### **Suggested Reviewers**

**Suggest names of individuals who would be particularly suited to assess the**

**proposed research.**

Erik Draeger

## Section 9: Testbed Resources

### Question #1

*The ALCF and OLCF have test bed resources for new technologies, details below. If you would like access to these resources to support the work in this proposal, please provide the information below. (1 Page Limit)*

*The OLCF Quantum Computing User Program is designed to enable research by providing a broad spectrum of user access to the best available quantum computing systems, evaluate technology by monitoring the breadth and performance of early quantum computing applications, and Engage the quantum computing community and support the growth of the quantum information science ecosystems. More information can be found here: <https://www.olcf.ornl.gov/olcf-resources/compute-systems/quantum-computing-user-program/quantum-computing-user-support-documentation>.*

*The ALCF AI Testbed provides access to next-generation of AI-accelerator machines to enable evaluation of both hardware and workflows. Current hardware available includes Cerebras C-2, Graphcore MK1, Groq, Habana Gaudi, and SambaNova Dataflow. New hardware is regularly acquired as it becomes available. Up to date information can be found here: <https://www.alcf.anl.gov/alcf-ai-testbed>.*

**Describe the experiments you would be interested in performing, resources required, and their relationship to the current proposal. Please note, these are smaller experimental resources and a large amount of resources are not available. Instead, these resources are to explore the possibilities for these technologies might innovate future work. This request does not contribute to the 15-page proposal limit.**

testbed.pdf

The attachment is on the following page.

No testbed resources are requested.