Project Title: Non-Adiabatic Electron-Ion Dynamics and Electronic Stopping

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Executive summary:

Rapidly advancing high-performance super computers such as Blue Waters allow for calculating properties of increasingly complex materials with unprecedented accuracy. In order to take full advantage of leadership-class machines, modern codes need to scale well on hundreds of thousands of processors. Here, we demonstrate high scalability of our recently developed implementation of Ehrenfest non-adiabatic electron-ion dynamics that overcomes the Born-Oppenheimer approximation. We find excellent scaling on up to 1 million floating-point units. As a representative example of material properties that derive from quantum dynamics of electrons, we demonstrate the accurate calculation of electronic stopping power, which characterizes the rate of energy transfer from a high-energy particle to electrons in materials. We use the example of a highly energetic hydrogen particle moving through crystalline gold to illustrate how scientific insights can be obtained from the quantum dynamics simulation and we perform exploratory research on secondary-electron emission.

Description of research activities and results:

Modern materials science relies not just on cutting-edge experimental techniques and accurate theoretical modeling, but it inherently incorporates computational simulations and computer experiments into its "toolbox". Length scales of interest reach from macroscopic dimensions all the way to atomistic resolution. In order for computational materials design to succeed, oftentimes it is crucial to develop a thorough understanding of the interaction of ions and electrons: The photon absorption of solar cells, radiation damage in materials, and secondary-electron emission are merely a few of many examples of properties or phenomena that have their roots in the physics of interacting electrons and ions.

The physical laws that govern this regime are well known: The behavior of electrons is governed by the many-body Schrödinger equation, which is a multi-dimensional differential equation. A direct solution of this equation is, however, exponentially complex, and obtaining the exact solution is intractable even using today's supercomputers, except for some simple atoms or small molecules. Scientists thus rely on physical and numerical approximations to predict material properties and for computing the electronic structure from the quantum-mechanical equation. The accuracy of quantum-mechanical calculations inevitably depends on these underlying approximations involved in the computation. With the recent advent of high-performance computers such as Blue Waters, quantum-mechanical calculations can now employ less restrictive approximations and, at the same time, be used to study highly complicated materials of today.

In many first-principles molecular dynamics approaches, computational cost is reduced by "coarse-graining out" the quantum dynamics of electrons. Electrons are then assumed to simply follow the movement of the ions instantaneously (adiabatic Born-Oppenheimer approximation). However, this approximation necessarily neglects the physics arising from the coupled quantum electron-ion dynamics, which is why various interesting properties are not accessible: An accurate description of electron dynamics is essential for addressing a wide range of interesting technological and scientific problems such as photo-catalysis, scintillators, or radiation shielding in space.

Therefore, an accurate description of electron dynamics through time-dependent quantum-mechanical theory is an important challenge today. While modern high-performance supercomputers help us tackle this grand challenge, their massively parallel and hybrid architecture, that is based on conventional central-processing units, but also graphic chips and many integrated cores, constitutes new challenges for numerical simulations. It is necessary to develop theoretical and algorithmic methods that are capable of fully exploiting current and future supercomputers, for instance for electronic-structure calculations.

We recently developed and implemented a first-principles computational methodology to simulate non-adiabatic electron-ion dynamics on massively parallel super computers. The scheme is based on the time-dependent extension of density functional theory along with the Kohn-Sham equations. Using an explicit, fourth-order Runge-Kutta integration scheme in the context of a plane-wave code we are now able to integrate the time-dependent Kohn-Sham equations in time, which allows us to explicitly study electron dynamics. We compute Hellman-Feynman forces from the time-dependent (non-adiabatic) Kohn-Sham states and propagating the ions according to these forces corresponds to Ehrenfest dynamics. We

showed that our implementation of this approach into the Qbox/qb@ll code is accurate, stable, and efficient; using the computational power of Blue Waters we were able to show excellent scaling of our implementation.

Thanks to the novelty of this new implementation, we are now able to pursue two important directions: (i) Exploring the scalability and the applicability of the code in the context of high-performance computing. (ii) Application of the code to elucidate the physics of electronic stopping in a material under particle-radiation conditions, which is a highly non-adiabatic process and, hence, crucially relies on overcoming the Born-Oppenheimer approximation.

Regarding the first goal, leadership-class machines such as Blue Waters are essential as they pave the way towards an exascale future. Using as many as 251,200 compute cores on Blue Waters are important tests that allow us to explore the limits of our parallel implementation. At the same time, since we found the scaling to be excellent, machines such as Blue Waters will allow us to tackle exciting large-scale scientific problems in the future. As a first example, we started exploratory research on secondary-electron emission from aluminum upon impact by a hydrogen particle. We plan to develop those results into a full proposal in the future.

By studying the scientific problem of computing the electronic stopping of a hydrogen projectile in crystalline gold material, we were able to unravel the influence of the stopping geometry and to understand contributions of semi-core electrons of the gold atoms, especially for highly energetic hydrogen projectiles. The good agreement with experiment demonstrates that this approach indeed captures the key physics and even promises predictive accuracy that will be beneficial for yet unexplored systems. In this context, it is crucial to use machines such as Blue Waters in order to check the computational parameters such as the plane-wave basis set, the super cell size, and to study long enough trajectories in order to eliminate computational artifacts. For the example of hydrogen projectiles in gold we were able to show that we can achieve this challenging goal. In particular, the influence of the stopping geometry (i.e. the path on which the projectile atom travels through the crystal) is a crucial aspect of the problem that is often difficult to access in experiments. This application may enable first-principles design and understanding of radiation hard materials as well as the processes that underlie scintillators and radiation shielding.

In summary, we achieved a highly scalable and highly accurate implementation of non-adiabatic electron dynamics based on real-time time-dependent density functional theory. We explored the performance of this code on Blue Waters finding excellent scaling. We obtained accurate scientific results for the electronic stopping contribution of crystalline gold impacted by a hydrogen atom in excellent agreement with experiment, proving the predictive capabilities of this scheme. Finally, we obtained preliminary data for secondary-electron emission from aluminum.

List of publications:

A. Schleife, E. W. Draeger, V. M. Anisimov, A. A. Correa, Y. Kanai; “Quantum Dynamics Simulation of Electrons in Materials on High-Performance Computers.”; Comput. Sci. Eng. (in press, 2014), Special Issue on "Leadership Computing".