Prospectus for:

Simulating the generation, evolution and fate of electronic excitations in molecular and nanoscale materials with first principles methods.

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Team members.

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Role: Parallelization for leadership class computing

Overview.

There are strong existing limitations on calculations of bound excited states in large molecules, and for resonance states in any polyatomic molecule. These limitations partly reflect deficiencies of existing software and algorithms. But more fundamentally they also reflect limitations of existing methods and models, particularly for resonances, or where multiple electrons are excited, or strong electron correlations are in play. The overall goal of this project is to make meaningful progress by coupling new and improved models for bound and metastable excited states from physical scientists with advances on underlying methodological challenges in applied mathematics, and practical realization via high performance computing.

Physical sciences challenges

There are three principal objectives associated with the chemical sciences. First is the development of new methods and associated software implementations for simulating bound excited states of large molecules (up to the 200-500 atom regime), including systems where strong electron correlations are important, as well as dynamic correlation. The potential benefit is that while there are existing methods that can achieve good accuracy for such states of small molecules, these new methods open up a new range of large-molecule applications, which include aspects of the photophysics and chemistry associated with natural and artificial light harvesting that are not yet well understood. The second goal is the adaptation of electronic structure methods to permit the simulation of resonance states of polyatomic molecules, where

an electron will autodetach. The potential benefit is that no capability of this type currently exists, despite the fact that interesting systems ranging from radiation-induced damage to DNA, the electron dynamics probed in experiments using new attosecond light sources, and the lowest excited states of various biochromophores involve resonances. The third objective is the development of reduced scaling implementations of existing coupled cluster methods for electronic excited states. The potential benefit is the ability to apply these reliable and proven methods for calculating excited states to larger molecules than was previously possible, and the potential ability to apply the same underlying ideas for reduced scaling to other methods, such as those in the first two objectives.

Computer science challenges

There are three principal objectives associated with the computer science that constitutes a complementary, enabling part of this project. The first goal is the development and refinement of an object-oriented tensor library, both for the traditional real matrices associated with theories of bound excited states, and for the complex matrices that naturally arise in treating resonance states. This goal is needed to permit the efficient implementation of the methods discussed in the three chemical sciences objectives, within a unified framework that is immensely easier and more extensible than a procedural approach. The second goal is to exploit this extensibility by parallelizing the tensor library using a distributed hybrid approach (MPI+threads) that is targeted for deployment on leadership class computers (but is also flexible enough to perform well on mid-range clusters). This is necessary to enable achievement of the application goals that are targeted for bound and resonance excited states. The third computer science goal is the distribution and propagation of the software that is developed under this work, both as an open source library for developers, and also as a significant update to a widely used, fully integrated simulation package for end-users of the application.

Applied mathematics challenges

There are also three principal objectives associated with applied mathematics that underpin these excited state methods, and also underpin the tensor libraries used to implement them. First is the exploration and implementation of rank reduction and compression schemes for the tensors that arise in excited state electronic structure calculations, and their use to develop reduced scaling excited state methods. This development in the framework of the tensor library will permit the new implementations that have much lower scaling of computational cost with molecular size, without affecting high-level codes. The second objective is the deployment of optimally efficient eigensolvers for the symmetric real eigenvalue problems that yield bound excited state energies, and the extension and development of eigensolvers for the complex eigenvalue problems that arise in treating resonance states. These developments are needed to permit efficient implementation of both classes of method. The third objective is the deployment and further development of robust linear solvers and effective preconditioners to underpin the iterative eigensolvers discussed above. This development is necessary to ensure overall efficiency of the excited state simulation methods developed here.