"Fast Solvers for Density Functional Theories"

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Summary

We are pursuing the use of the finite element method for density functional theory calculations. Our current method augments the FEM basis with local atomic orbitals that are known to reproduce the physics well to reduce the size of the FEM basis. The resulting method will give converged basis set accuracy with manageable matrix sizes. Moreover, the matrices will have a very high degree of sparsity, making the design of sparse eigensolvers much simpler than with local basis sets. We are nearly finished with the paper Dynamical Systems and Non-Hermitian Iterative Eigensolvers. This paper draws an isomorphism between dynamical systems and a class of preconditioned iterations for large-scale eigenvalue problems, including non-linear eigenvalue problems.

Overview

Density functional theory encompasses a group of methods for investigating the chemical bonding of molecules and materials, and can predict a host of important properties such as chemical reactivity and stability, electronic properties, optical absorption and spectroscopic properties, and many other. Most techniques in these methods have to solve an eigenproblem arising from the time-independent Schrodinger equation for the electronic wave function.

Our work under the ASCR program has focused on finding faster eigensolvers, or eigensolver replacements, for density functional theory. To date we have looked at DFT methods that use local atomic-orbital-like basis set expansions to describe the eigenvectors. This expansion results is relatively small basis set sizes, but without much overall sparsity in the resulting matrices.

Finite Elements in DFT

We have begun exploration of finite element methods (FEMs) to augment local basis sets. FEMs, of course, have a long history in continuum mechanics. Their use in quantum DFTs has been limited because typically extremely large numbers of elements have been required to describe the core electrons. Our current approach is significantly different: In collaboration with John Pask (LLNL), we are developing a technique that uses the classic methods from atomic and molecular physics to solve atomic wave functions on radial grids, and then only uses the finite element basis to augment these solutions in the bonding region. Several

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things recommend this hybrid approach. Although larger than a purely local orbial calculation, the overall basis set size is much smaller than for a pure FEM approach. Moreover, there is significantly more sparsity than found in either local basis set approaches or in plane wave approaches. Our aims are to (1) develop high-quality atomic solvers for all-electron atoms and atoms with pseudopotentials, and (2) develop fast generalized eigensolvers that can take advantage of the sparsity in this new basis set. We are well on the way to our first goal, having developed a suite of techniques including shooting methods, pseudospectal, and finite element methods to solve the one-dimensional spherical atomic Schrodinger equation on a variety of different radial grids.

Dynamical Systems and Iterative Eigenproblems

We have also identified an equivalence between some discrete dynamical systems and a class of preconditioned iterations for the non-Hermitian eigenvalue problem. This connection provides a framework for investigating the convergence and stability of certain existing eigensolvers and suggests new algorithms. Although not developed as an algorithm for the algebraic eigenvalue problem, the Car–Parrinello method from quantum molecular dynamics determines the Kohn–Sham eigenstates from a second order ordinary differential equation (Newton's equations of motion): the Car-Parrinello method allows the solution of the iterative eigenvalue problem in a single step by taking advantage of the isomorphism to the equations of motion. However, achievement of this solution involves a certain amount of trial and error determination of preconditioning factors in the form of a "fictitious mass" for propagating the electronic wave function. In exploring the isomorphism with the iterative eigenvalue methods, we may suggest more rigorous methods for preconditioning the associated equations, allowing significant improvements in the speed and stability of the solutions to quantum DFTs.

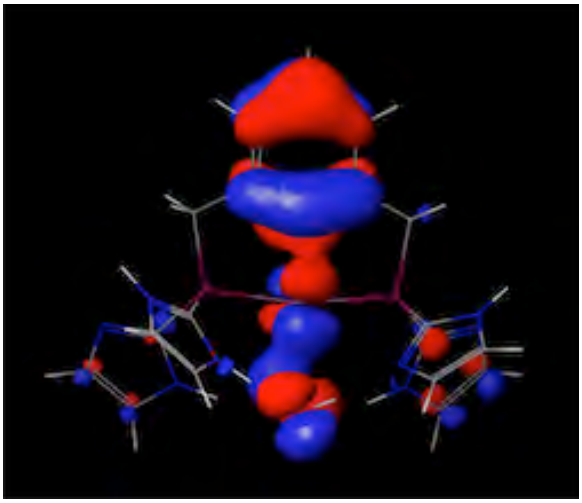

Figure 1: Bonding orbital between an organopalladium catalyst and molecular oxygen. The bonding orbital is one of the eigenvectors we seek solutions for, and the nature of this solution determines the strength and shape of the chemical bond.

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