Density Matrix Methods as Eigensolver Replacements in Electronic Structure Theory

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Summary

The eigensolver step is the computational bottleneck in many approaches for computation of the electronic structure of materials and molecules. We are pursuing replacements for the eigensolver using density matrix-based approaches. Our recent work has focused on density matrix purification in a Lanczos subspace, and shows great promise for accelerating this step in the computation.

Electronic structure theory is 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. The eigenproblem can be isolated, in tight-binding and extended Huckel techniques, or part of a self-consistent field sequence of iterations, in Hartree-Fock and density functional theory techniques. The last 20 years has seen great amounts of success in accelerating other parts of electronic structure theory calculations, but has had little success accelerating the eigensolver, and this step is now the computational bottleneck in the majority of problems.

One attractive alternative comes from realizing that the eigenvectors themselves are often not required as much as the density matrix, which is a projection operator for the space spanned by the occupied electrons, made by multiplying the occupied eigenvectors with themselves. *Density matrix methods* are approaches that can form the density matrix directly without requiring an eigensolver step. These approaches typically require an iterative sequence of matrix-matrix multiplies. From a practical perspective, these approaches are interesting techniques because the matrix multiply operation is typically easier to parallelize and take advantage of sparsity than the eigensolve operation. From a theoretical perspective, they are interesting because of the obvious parallels between these techniques and subspace iteration techniques in linear algebra, and investigation of these parallels may lead to superior convergence and performance of the techniques.

Our work to date has focused on density matrix purification, which uses the facts that a proper density matrix is idempotent (it is a projector for the subspace spanned by the occupied eigenvectors), has a trace equal to the number of electrons, and commutes with the total energy operator, to purify an initial guess to the density matrix until it is correct. Not only is density matrix purification significantly faster than other density matrix approaches, they are also mathematically

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much simpler. Purification techniques seek to build the projector operator by an iterative sequence of matrix squares and shifts that ultimately converges on a projector that has the proper trace (corresponding to the number of electrons).

Our current work attempts to develop density matrix purification techniques within a Lanczos subspace.

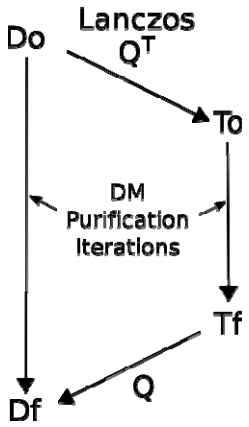

Figure 1: Density matrix purification in a subspace.

Figure 1 shows a schematic of our current approach. The arrow on the left maps the initial density matrix to the final matrix using the standard density matrix purification approaches. In our current approach (the 3 arrows on the right) we first use a length Lanczos transformation to convert the current density matrix **D** to the Lanczos subspace representation **T**. We then apply the density matrix purification iterations to this matrix, and then use the matrix **Q** to transform the final subspace density matrix $\mathbf{T}_f$ to the density matrix $\mathbf{D}_f$.

Our preliminary results are promising but uneven. In several test cases we see great acceleration of the subspace purification approach over the standard density matrix purification approach. However, we also see other test cases where loss of orthogonality occurs among the Lanczos vectors. We are currently investigating selective orthogonalization schemes to determine whether such an approach can stabilize the convergence and still preserve the speed gains.

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