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Scalable methods for electronic excitations and optical responses of nanostructures: mathematics to algorithms to observables

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1 Objectives and highlighted accomplishments

The master project under which this work is funded had as its main objective to develop computational methods for modeling electronic excited-state and optical properties of various nanostructures. The Minnesota team was comprised of two collaborating groups: The first directed by Jim Chelikowsky from the dept. of Chemical Engineering and Materials Sciences (Now at the university of Texas at Austin), and the second under the direction of Yousef Saad, from the department of computer science and engineering. The specific goals of the computer science group were primarily to develop effective numerical algorithms in Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TDDFT). There were essentially four distinct stated objectives. The first objective was to study and develop effective numerical algorithms for solving large eigenvalue problems such as those that arise in Density Functional Theory (DFT) methods. The second objective was to explore so-called linear scaling methods or Methods that avoid diagonalization. The third was to develop effective approaches for Time-Dependent DFT (TDDFT). Our fourth and final objective was to examine effective solution strategies for other problems in electronic excitations, such as the GW/Bethe-Salpeter method, and quantum transport problems.

The following is a list of a few highlighted accomplishments for the duration of the project. Section 2 presents details on selected topics.

1. The project begun with an investigation on the effective use of planewave methods for TDDFT. We developed a new, FFT-based, Time-dependent Density Functional Theory code for TDDFT which attained a factor or 20 to 35 over our earlier code which worked entirely in real-space, see [11].

2. In the course of exploring TDDFT, we investigated the solution of related Helmholtz equations [12] and proposed a number of effective strategies for solving indefinite complex linear systems.

3. Along with Bernard Philippe (University of Rennes, France), we considered domain-decomposition type methods for solving eigenvalue problems [13]. This work provided some useful insight into the Automatic Multi-level Substructuring methods.

4. We wrote an exhaustive review paper [17] on numerical methods for electronic structure calculations for the SIAM review journal. Another survey-type article [6] reviewed our work in the area of TDDFT.

5. One of the most significant accomplishments in the work supported by this grant is our work on Chebyshev- subspace iteration [22]. The method proposed in [22] represented a significant departure from our classical approach by merging the diagonalization loop with the nonlinear self-consistent loop. Typically, this work resulted in a factor of 10 speed-up or more for large systems.

6. The algorithm and codes resulting from the above contribution enabled us to perform calculations that were not possible before. Among these is our work on magnetism in iron [18], and the study of vibrational and other properties evolutive properties of nanocrystals [8, 7, 9].

7. We have continued to develop and expand the capabilities of our code PARSEC - in particular periodic systems were treated [1]. At the same time we developed a matlab version of PARSEC, named RSDFT, geared toward educational and prototyping use.

8. Various strategies were tested for eigenvalue calculations [19, 20, 22, 21].

9. In a collaboration with Stefano Baroni (SISSA, Trieste, Italy) we developed a method based on the Lanczos algorithm for performing Time-Dependent Density Functional Theory calculations [2, 15]. This work generated quite a good number of citations in the literature.

2 Research contributions

Fast TDDFT using planewave bases. The project started with the development of a novel, FFT-based, Time-dependent Density Functional Theory code. This code attained a factor or 20 to 35 over our earlier implementation which worked entirely in real-space. This gain was achieved by (1) using a new algorithm (2) better optimization of the technique. The paper appeared in [11].

Efforts in Diagonalization algorithms. One of the main objectives of the project was to find methods for reducing the cost of diagonalization by using algorithms that are specifically tailored to the situation of DFT. The main efforts in this direction were based on a number of observations. First, we observed that most electronic structures calculation codes focus too much on computing individual eigenvalues accurately while what matters is simply to have a good basis (typically orthogonal) of the invariant subspace associated with the occupied states. Focussing on eigenvalues and eigenvectors, will tend to require costly algorithms, primarily because diagonalization codes demand repetitive orthogonalizations to get accurate eigenvectors. This is the situation for our earlier code and of the widely used code ARPACK. It is not too uncommon for orthogonalization to consume 90% of the time spent in a typical DFT code. In fact, it is even possible to avoid computing eigenvectors altogether and this constitutes the main foundation of so-called order n, or linear scaling, methods. The second basic observation we made is that the problem under consideration is really a nonlinear eigenvalue problem and it is solved as a sequence of linear eigenvalue problems only for historical reasons (simplicity of the self-consistent iteration).

We have explored and tested a number of new options for diagonalization in our real-space DFT code (PARSEC) including the following:

1. Block Davidson methods [21]. The goal of this approach was to exploit information previous self-consistent iterations. The results were good but the improvements did not warrant an inclusion in PARSEC.

2. A Chebyshev-Davidson algorithm [20]. This technique exploits a Chebyshev filter with the idea of reducing the cost of orthogonalization.

	Partial Lanczos				ARPACK			
n_o	MATVECS	REORTHS.	MEMORY MB	secs	MATVECS	RESTARTS	MEMORY MB	secs
248	3150	109	2268	2746	3342	20	357	16454
350	4570	184	3289	5982	5283	24	504	37371
496	6550	302	4715	13714	6836	22	714	67020

Table 1: Costs for Partial Lanczos and ARPACK for $Ge_{99}H_{100}$. This matrix is a Hamiltonian in real-space which arises from the similation of a Germanium cluster (99 Ge Atoms, 100 H atoms). Its size is $n = 94,341$, and it has nnz=633,2795 nonzero entries. The number of occupied states is 248. The table compares various costs for the situtations when subspaces of dimension 248 (the minimun required), 350, and 496 are computed. The algorithm is about 6 times faster than ARPACK for the first 2 cases, which are the more practical ones.

3. The idea of filtered iteration was taken a little further by selecting the filter polynomial more carefully. Specifically we considered least-squares polynomials which approximate a step function. The step function has value one for occupied states and zero elsewhere. Two articles have been published on this general idea: [4, 16].

4. Lanczos algorithm with partial reorthogonalization [5]. The main point of this study was to show that by focusing on the convergence of the invariant subspace instead of individual eigenvectors, one can reduce the cost of "diagonalization" in a significant way. This is due mainly to the reduction of the orthogonalization costs since the Lancozs algorithm can be used with partial reorthogonalization instead of full reorthogonalization. A gain of a factor of up to 7 can be made in the cost of diagonalization at the expense of using more memory. In [5], it was argued that for the problems generally under consideration, memory is still not a major issue. In addition, it is also possible to exploit secondary storage in case memory were to become a bottleneck. An illustration is shown in Table 1.

5. Finally, we also did some work on Block-Schur methods for symmetric eigenvalue problems as a means to take advantage of eigenspaces from previous iterations in the self-consistent loop in DFT codes [21].

Efforts in linear-scaling methods. In [3] we investigated the issue of generating the charge density without the availibility of eigenvalues and eigenvectors. As is well-known in Density Functional Theory, the charge density can be viewed as the diagonal of a certain projector (the density matrix) which is simply the spectral projector associated with the occupied states. This is one of the main ingredients used in so-called order-n methods. The paper [3] considers a number of new ways of estimating the diagonal of a matrix, when the main operation is the matrix-vector product.

Chebyshev Subspace iteration. A major development in this project took place toward the beginning of the 3rd year. We re-examined again the idea of filtering and this resulted in a new algorithm which yielded a major improvement both in reducing cost and in improving robustness of our real-space code. This particular contribution [19, 22] had a good impact on the field.

The idea we explored was simply to *merge diagonalization loop with the nonlinear loop.* This idea stems from the viewpoint mentioned above that the overall problem is a nonlinear problem, so it is wasteful to compute eigenvalues accurately. Instead, the idea is to perform of a subspace iteration whereby some initial subspace is improved by a Chebyshev filter at each self-consistent iteration. The main difference with standard diagonalization is that we do not iterate the basis to convergence. Instead, we let the nonlinear iteration take care of the convergence. We have seen cases where the gain in time when compared with a standard package such as ARPACK is as high as 15. A parallel version of the code was developed and this became the default eigensolver in PARSEC [22].

Acceleration techniques for nonlinear problems. This work was motivated by the problem in electronic structure calculations, whereby a fixed point iteration, known as the Self-Consistent Field (SCF) iteration, is accelerated by various strategies termed 'mixing'. Our specific goal here was to improve

method	# MV products	# SCF steps	total energy	CPU (secs)
ChebSI	114526	10	-77.316873	8870.10
ARPACK	142047	10	-77.316873	62026.37
TRLan	145909	10	-77.316873	26852.84

Table 2: This test is for a silicon cluster of 525 silicon atoms passivated with 276 hydrogen atoms ($Si_{525}H_{276}$). The matrix size is $n = 292,584$ and the number of occupied states (eigenvectors to be computed) is 1,194. The table compares 3 methods used. The first is the new method which does not focus on eigenvectors (using Chebshev filters of degree 8). The other two are based on standard diagonalization and utilize the well-known ARPACK package and a competitive algorithm called Thick Restart Lanczos (TRLan) developed by H. Simon and Kesheng Wu from LBL. Times shown are for the whole self-consistent iteration. As can be seen, in all cases, the code takes 10 outer (SCF) iterations to converge. Notice that the number of matrix-vector operations is only marginally reduced for ChebSI relative to the other two methods. However, the overall cost is about 7 times less than that obtained with ARPACK.

the acceleration schemes used in our real-space code PARSEC, both from the point of view of robustness and that of speed. We explored two classes of multisecant methods which allow to take into account a variable number of secant equations at each iteration. The first is the Broyden-like class, of which Broyden's family is a subclass, and Anderson mixing is a particular member. The second class is that of the nonlinear Eirola-Nevanlinna-type methods. The codes resulting from this study have been incorporated into PARSEC. A paper that described this work was published in the literature [14].

Solving complex systems in Transport. We considered the solution of sparse linear systems that arise from the application of real space pseudopotential methods in the study of electron transport properties of nanoscale junctions. These problems give rise to linear systems of equations with complex variables which are difficult to solve by standard iterative methods. We analyzed the performance of a few preconditioners for solving these complex linear systems which originate from the application of real space pseudopotential methods in the study of electron transport properties of nanoscale junctions. These linear systems of equations are part of a self-consistent loop to compute the charge density and corresponding potential at the junctions. The coefficient matrices for these systems have a regular structure with two dense blocks associated with boundary conditions. These dense blocks cause difficulties to general preconditioners, due to the amount of fill-in which they tend to generate. The preconditioners studied were of the general-purpose kind, such as ILU with threshold (ILUT), ILU with level of fill (ILUK), and the Algebraic Recursive Multilevel Solvers (ARMS). The study shows that ARMS with diagonal dominance – based nonsymmetric ordering (ddPQ) is generally more robust than the other preconditioners which were tested.

We also studied systems which are of the same type but which are easier to work with. Indeed, the wave-like nature of the problem yields systems that are somewhat similar to the systems obtained from the Helmholtz equations. We have developed some new strategies which perform quite well for Helmoltz equations.

TDDFT from a Liouville operator perspective. In a collaboration with Stefani Baroni's team from SISSA in Trieste (Italy) we explored Lanczos-type algorithms for Time-Dependent Density Functional Theory (TD-DFT) calculations. A method developed by Baroni and his group expresses the problem in a form which can be viewed as that of solving a sequence of linear systems with a shifted matrix. The number of shifts can be large so the best candidate for this type of calculation is an adaptation of the Lanczos algorithm. However, as the shift (which corresponds to frequency) gets well inside the spectrum, the performance of the Lanczos algorithm deteriorates. The method consisted essentially of running the nonsymmetric algorithm without reorthogonalization and computing the wanted quantities from the resulting sequence of vectors. This new implementation of time-dependent density-functional theory allows the *entire* spectrum of a molecule or extended system to be computed with a numerical effort comparable to that of a *single* standard ground-state calculation. The method is particularly well suited for large systems and/or large basis sets, such as

plane waves or real-space grids.

The method uses a super-operator formulation of linearized time-dependent density-functional theory. It represents the dynamical polarizability of an interacting-electron system as an off-diagonal matrix element of the resolvent of the Liouvillian super-operator. One-electron operators and density matrices are treated using a representation borrowed from time-independent density-functional perturbation theory, which permits to avoid the calculation of unoccupied Kohn-Sham orbitals. The resolvent of the Liouvillian is evaluated through the non-symmetric Lanczos method. Each step of the Lanczos recursion essentially requires twice as many operations as a single step of the iterative diagonalization of the unperturbed Kohn-Sham Hamiltonian. Suitable extrapolation of the Lanczos coefficients allows for a dramatic reduction of the number of Lanczos steps necessary to obtain well converged spectra, bringing such number down to hundreds (or a few thousands, at most) in typical plane-wave pseudopotential applications. The resulting numerical workload is only a few times larger than that needed by a ground-state Kohn-Sham calculation for a same system. Two consecutive papers were published describing this work [2, 15].

3 Personnel

This grant provided partial or full support for the following researchers during the duration of the project:

1. Suzanne Shontz [post-doc associate 2004-2006]
2. Costas Bekas [post-doc associate 2003-2005]
3. Prakah Dayal [post-doc associate 2006-2007]
4. Daniel Osei-Kuffuor [graduate student 2004-2007]
5. Haw-ren Fang [post-doc associate 2006-2008]
6. Adam Jundt [graduate student 2006-2007]

Among the above, Suzanne Shontz is currently a faculty member at Penn-State university (recipient of a PECASE award in 2011), Daniel Osei-Kuffuor is a researcher in Lawrence Livermore Lab., and Costas Bekas is at IBM Zurich (team member recipient of a recent Gordon Bell Award).

4 Software

Some of the techniques developed during the project were retrofitted into our code PARSEC. In addition, we also devoted some effort in developing a matlab version of our real-space electronic structures code. This code, called RSDFT, has been assembled by a team of physicists, and computer scientists, including several undergraduate students (not supported by this grant) who worked as summer interns. It is targetted at an audience of mathematicians and computer scientists.

5 Publications

An updated list of technical reports and articles published under this grant is given in the references. All papers are available online under the "research reports" link of:

http://www.cs.umn.edu/∼saad

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