MADNESS Applied to Density Functional Theory in Chemistry and Nuclear Physics

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Abstract. We describe some recent mathematical results in constructing computational methods that lead to the development of fast and accurate multiresolution numerical methods for solving quantum chemistry and nuclear physics problems based on Density Functional Theory (DFT). Using low separation rank representations of functions and operators in conjunction with representations in multiwavelet bases, we developed a multiscale solution method for integral and differential equations and integral transforms. The Poisson equation, the Schrodinger equation, and the projector on the divergence free functions provide important examples with a wide range of applications in computational chemistry, nuclear physics, computational electromagnetic and fluid dynamics.

We have implemented this approach along with adaptive representations of operators and functions in the multiwavelet basis and low separation rank (LSR) approximation of operators and functions. These methods have been realized and implemented in a software package called Multiresolution Adaptive Numerical Evaluation for Scientific Simulation (MADNESS).

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1. Introduction

It was already clear in [4, 5] that multiresolution representations of functions and operators should lead to useful numerical algorithms. However, the straightforward generalization of such an approach from one spatial dimension to higher dimensions yields algorithms that are too costly for practical applications. The development of efficient and robust algorithms using multiresolution analysis (MRA) for solving partial differential and integral equations in three and higher dimensions has only recently been successfully applied [6, 13, 14, 15]. These algorithms rely on low separation rank representation and tools for representing a particular class of approximations using Gaussian functions [7, 8, 9, 15]. The LSR can be thought of as an extension of the separation of variables approach where the correlation between functions (i.e. basis functions) is small they form well separated groups of functions the of size of the

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groups is the rank. The combination of an truly orthogonal adaptive approach combined with LSR produces a method that scales nearly linearly with increasing basis functions as well as significantly reducing the memory storage costs.

Approximations involving gaussians have a long history in quantum chemistry and in nuclear physics, starting with [10, 18, 17]. Typically gaussians (usually with an additional polynomial factor) are used to approximate the atomic wave functions, including their cusps. More recently, an approximation by Gaussians of the function $1/r$ (Coloumb potential) along with the error analysis has been considered in [16, 11].

In our approach we use Gaussians to construct separated representations of Green's functions as the initial step in obtaining an efficient multiresolution representation. In [6, 13, 14, 15] we developed an MRA approach (using multiwavelet bases) which incorporates the advantages of adaptive refinement in representing functions and operators, guaranteed solution for arbitrary (finite) precision along with computationally fast algorithms. The speed of our algorithms is comparable to that of the Fast Multipole Method (FMM) [12]. In fact, the approximation technique used in our approach and that in FMM are related but this topic is beyond the scope of this paper. We only note that our approach has advantages in higher dimensions.

Our approach, described in [9, 15], is applicable to a wide variety of kernels, including singular kernels such as the projector on the divergence free functions and some oscillatory kernels, e.g., the Helmholtz kernel $\frac{e^{-ikr}}{r}$, where kr is moderately large in the region of interest. As a result, our approach opens up new opportunities in constructing effective numerical methods and provides a way of developing practical operator calculus in high dimensions. In particular, we are working on constructing multiparticle Green's functions and spectral projectors. In this paper we briefly summarize some of our recent work and that of our collaborators in systematically applying MRA and LSR approximations to problems in computational quantum chemistry and nuclear physics. We also outline current research and new directions that originate in our approach.

For a non-relativistic system of electrons and nuclei, the time-independent Schrodinger equation is given by

$$\mathbf{H}\Psi = E\Psi \tag{1}$$

where E is the energy for each wave function Ψ. Mathematically, the normalized Hamiltonian $\mathbf{H}$ is of the form

$$\mathbf{H} = -\sum_{i=1}^{N} {\nabla_i}^2 + V \tag{2}$$

where the first sum is the kinetic energy operator and the second term represents the potential energy terms such as the coulomb, electron-electron and nuclei-electron repulsions, and the quantum mechanical effects of electron exchange and correlation. In electronic structure calculations the first term represents the kinetic energy of the electrons while in nuclear physics their are two kinetic energy operators one for the electrons and one for the nuclei. In addition, the potential in nuclear physics does not contain a Coloumb type term but can contain high gradients and the potentials are often not determined from first principles but rather are derived empirically.

Our approach recasts the Schrodinger eigenproblem in 3-D as an integral equation,

$$\Psi = -G(V\Psi) \tag{3}$$

where

$$(G * f)(r) = \int \frac{e^{-k|r-s|}}{4\pi|r-s|} f(s)ds. \tag{4}$$

This permits us to solve the eigenproblem iteratively using fixed-point iteration with controlled accuracy by using the MRA and LSR approaches.

2. Low Separation Rank Representation

At the heart of our computational method is the representation of the operator and functions in the singular and the oscillatory regions by their low separation rank approximations. The separated representation of a multivariable function f can be written as,

$$||f(x_1, x_2, ...x_n) - \sum_{l=1}^{r} s_l \varphi_1^l(x_1)\varphi_2^l(x_2)\dots\varphi_n^l(x_n)|| \leq \epsilon. \tag{5}$$

where the desired accuracy ϵ is an input to the calculation and the the functions $\{\varphi_i^l(x_i)\}$ and coefficients $\{s_l\}$ are adjusted to achieve this accuracy with a minimal separation rank r. In the same manner, we approximate multidimensional operators as a sum of products of operators acting in each direction separately. The set of functions $\{\varphi_i^l(x_i)\}$ in (5) is not fixed and depends on the function f. The functions $\{\varphi_i^l(x_i)\}$ come from a family of functions that is typically too large to form a basis. Such an approach goes beyond the notion of a basis for representing functions; we note that the algorithms for constructing and maintaining (5) are necessarily nonlinear (see [7, 8, 9]).

In our current approach for the non-oscillatory Helmholtz kernel we use Gaussian functions e^{-pr^2}, where $p > 0$ and real for $\{\varphi_i^l(x_i)\}$ (5). We apply this approximation for the oscillatory Helmholtz kernel, i.e. e^{ikr}/r, where the functions $\{\varphi_i^l(x_i)\}$ in (5) are Gaussians, $e^{\tau r^2}$, and τ are complex-valued. For example, the real and complex part of the Helmholtz can be approximated, with an error of $1e-10$ using 52 terms for $k = 50$ and using 17 terms, respectively, from $[10^{-10}, 1]$.

3. Multiresolution Representations

We have chosen multiwavelets [1] as bases for multiresolution representation of operators in two and three dimensions. This choice properly addresses many (contradictory) requirements on such bases, namely, an accommodation of boundary conditions without a loss of order or conditioning of approximation, an efficient algorithm for point-wise multiplication as well as availability of scale-consistent analogues of forward and backward differentiation (see [2]). We start with the separated representation of the operator kernels, e.g. as in ([14]), and then construct a non-standard representation in the multiwavelet bases. The necessary estimates are available in [6] and corresponding algorithms were developed in [14, 15, 19, 20].

4. MADNESS

Multiwavelets were combined with low separation approximations using exponential functions for representation of functions and operators and implemented in dimensions 1, 2, 3, and 6 in our prototype software package Multiresolution Adaptive Numerical Evaluation for Scientific Simulation (MADNESS). The initial prototype version used Python as the programming environment enabling the application code to be written at a very high level in terms of operators and functions, rather than the more common explicit manipulation of sparse lists of integrals and matrices. A wide range of electronic structure capabilities were developed using this framework. In addition, exploratory work has been conducted in fusion and fluid dynamics. The prototype runs in parallel on shared-memory computers using fork-and-join communicating between processes via files.

A new production version of MADNESS is being implemented with a design goal of efficiently exploiting $O(10^6)$ processors for addressing large problems while retaining the high-level composition of applications. In effective one-particle (HF and DFT) calculations, there is one 3D molecular orbital per electron ($O(10^{2-3})$) each with an independent, adaptively-refined mesh. In effective two-particle calculations there is one 6D function per electron pair, and it is desirable to compute in up to at least 9D. In addition to enabling definitive benchmark results for the dynamics of few-electron systems, the ability to compute with electron pairs enables full

numerical solution of standard quantum chemistry methods such as second-order perturbation theory (independent, linear electron pairs) and coupled-cluster with single and double excitations (coupled, non-linear electron pairs). Localization of the orbitals is used to reduce the overall scaling of HF and DFT to linear in the number of electrons. C++ is used as the programming language and a new parallel runtime based upon futures and distributed containers is used to manage the coarse and medium grain parallelism and for recursive traversal of trees.

5. Results

Our prototype multiresolution MADNESS solver is implemented using PYTHON for high-level control and the languages C/C++/FORTRAN for computationally intensive operation. For the application to nuclear physics, the input potential is the Poschl-Teller-Ginocchio potential described in [3] where we are only solving for the S eigenstates. This potential is important in nuclear physics but the eigenvalues can be solved analytically providing a direct way of accessing the effectiveness. In 3D we used 9 multiwavelets and computed with a prescribed desired accuracy of $1.e-3$. The results are given immediately below.

Exact Value	Multiwavelet results
-39.7400	-39.7399
-18.8977	-18.8976
-0.3205	-0.3201

6. Current directions

Central to advancing the state of art in computing and, as a result, in quantum chemistry, materials science and physics, is computing in high dimensions. To this end, we are developing mathematical tools for making a transition from one-particle approximations (DFT, LDA, Hartree-Fock) to the two-particle approach. This requires computing in six spatial dimensions. Time dependent problems are also of interest and we are formulating several schemes with initial application to evolution of electronic systems in three and six dimensions. We are interested in generalizing results in [9] for computing (5) so that the family of functions $\{\phi_i^l(x_i)\}$ are Gaussians, $e^{-p_1 x_1^2} e^{-p_2 x_2^2} \cdots e^{-p_n x_2^2}$, where the exponents $p_1, p_2, \ldots p_n$ are allowed to be distinct in different directions. This will allow us to construct approximations to multiparticle Green's functions and spectral projectors. We also continue the work on general separated representations started in [7, 8].

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