Fast multiresolution methods for density functional theory in nuclear physics

G. I. Fann\textsuperscript{1}, J. Pei\textsuperscript{5, 6}, R. J. Harrison\textsuperscript{1, 4}, J. Jia\textsuperscript{1}, J. Hill\textsuperscript{1}, M. Ou\textsuperscript{2}, W. Nazarewicz\textsuperscript{5, 6}, W. A. Shelton\textsuperscript{1} and N. Schunck\textsuperscript{5, 6}

\textsuperscript{1} Computer Science and Mathematics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37830
\textsuperscript{2} UT Joint Institute for Computational Sciences, Oak Ridge, TN 37831
\textsuperscript{4} Department of Chemistry, University of Tennessee, Knoxville, TN 37996
\textsuperscript{5} Department of Physics, University of Tennessee, Knoxville, TN 37996
\textsuperscript{6} Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

E-mail: fanngi@ornl.gov

Abstract.

We describe a fast real-analysis based $O(N)$ algorithm based on multiresolution analysis and low separation rank approximation of functions and operators for solving the Schrödinger and Lippman-Schwinger equations in 3-D with spin-orbit potential to high precision for bound states. Each of the operators and wavefunctions has its own structure of refinement to achieve and guarantee the desired finite precision. To our knowledge, this is the first time such adaptive methods have been used in computational physics, even in 1-D. Accurate solutions for each of the wavefunctions are obtained for a sample test problem. Spin orbit potentials commonly occur in the simulations of semiconductors, quantum chemistry, molecular electronics and nuclear physics. We compare our results with those obtained by direct diagonalization using the Hermite basis and the spline basis with an example from nuclear structure theory.

1. Introduction

Solving the Schrödinger and the Lippman-Schwinger equations are important for understanding the chemistry and the nuclear structures of atoms and molecules. In this paper, we present a fast real-analysis based algorithm using an adaptive multiwavelet basis for solving the Schrödinger and Lippman-Schwinger equations with spin-orbit interactions for a non-spherically symmetric potential in 3-D.

It has been known for some time that multiresolution analysis (MRA) and multiwavelets should lead to useful numerical algorithms. However, straightforward generalizations of such an approach from one and two spatial dimensions to higher dimensions yield algorithms that are too costly for practical applications. The development of efficient and robust algorithms in three and higher dimensions has recently been successful. These algorithms rely on low-separation rank (LSR) approximations of weakly singular kernels coupled with MRA\textsuperscript{3, 5, 7}

In this paper we describe an extension of these ideas to solving the Schrödinger equation and the Lippman-Schwinger equation with spin-orbit interactions. The spin-orbit term is an important part of many quantum-mechanical Hamiltonians. For example, in chemistry, spin-orbit interaction models the shifts in an electron’s atomic energy levels, e.g. the splitting of
spectral lines. It also occurs in models of the effects of electric field or magnetic field on an electron’s spin and it is an important component of the strong forces acting between nucleons.

The spin-orbit interaction introduces rotational terms into the Schrödinger equation. In particular, terms involving the gradient of the potential and the gradient of the wave functions are introduced into the equation. In practice, physicists and chemists have been able to perform this computation, but it is difficult to obtain accurate eigenvalues and eigenfunctions beyond four to five digits in the general case.

The problem can be described as follows. Let \( H \) denote the Hamiltonian with eigenvalues \( E \) and eigenfunctions \( \phi \). The Schrödinger equation, with spin-orbit, is written as

\[
H\phi = E\phi
\]

where \( H = \left( -\frac{\hbar^2}{2m} \Delta + V \right) I + V_{SO} \) with \( I \) being the 2 \( \times \) 2 identity matrix, \( \Delta \) is the Laplacian operator, \( \hbar \) is Planck’s constant, \( m \) is the mass of the particle and \( V \) is a \( L_2 \) integrable compact scalar potential function.

The spin-orbit potential term, \( V_{SO} \), assuming reflection symmetry with respect to the \( y \)-axis, is an application of a 2 by 2 matrix operator on a vector-valued complex valued wavefunction \( \phi = (u, v)^T \), with \( u, v : \mathbb{R}^3 \to \mathbb{C} \). The operator \( V_{SO} \) is given by:

\[
V_{SO} := -i\lambda \left[ \frac{(\partial_y V)\partial_x - (\partial_x V)\partial_y}{(\partial_V\partial_x)\partial_x - (\partial_V\partial_y)\partial_y} \right]
\]

where \( \partial_\perp := i\partial_x + \partial_y, i := \sqrt{-1}, \lambda \) is a constant, and \( A^* \) denotes complex conjugation of \( A \). Each wave-function satisfies the zero Dirichlet boundary condition for a sufficiently large box or asymptotically.

A common spectral method for solving this eigensystem problem is to expand the wavefunctions and its first and second derivatives in a basis (e.g., harmonic oscillators, splines, Gaussians) of fixed length, form a linear eigensystem problem and solve for the eigenvalues and the eigenvectors. The coefficients of the wavefunctions form the entries of the unknown eigenvectors. Another common method is to numerically discretize the Hamiltonian operator. In both cases a dense or a sparse generalized eigensystem problem \( Hx = \lambda Sx \) is solved using a standard eigensolver, LAPACK for the dense case \([2]\), and typically Davidson or Lanczos eigensolvers for the sparse case \([4, 6]\).

Formally, we rewrite the Schrödinger equation as a Lippman-Schwinger equation:

\[
(H - E)\phi = (V - V_{SO})\phi.
\]

The formal inverse \( G = (H - E)^{-1} \) is the convolution operator with the bound-state Helmholtz kernel. We describe the application and approximation with this Green’s function below.

### 2. Multiwavelets and low-separation rank representations

The representation of functions and operators is based on an adaptive pseudo-spectral representation of functions and operators using the discontinuous Alpert’s multiwavelets\([1]\) and low-separation rank approximation of weakly singular kernels. The use of these representations for solving Schrödinger equation without spin-orbit potential in computational chemistry and density functional theory were presented in \([7, 8, 10]\). To represent functions in 3-D, we use tensor products of 1-D multiwavelets.
The kernel for the bound state Helmholtz convolution operator $e^{-kr}/r$ is approximated by LSR using Gaussians

$$\frac{e^{-kr}}{r} = \sum_{m=1}^{M} w_m e^{-p_1,m x_1^2} e^{-p_2,m x_2^2} e^{-p_3,m x_3^2} + O(\frac{\epsilon}{r}).$$

The number of terms, $M$ in the sum, is nearly optimal and depends logarithmically on precision $\epsilon$. In [3], we showed the compatibility of the fast application of low-separation rank approximation of the Helmholtz operators with the multiwavelet approximation of functions. The approximation of the Helmholtz kernel is tabulated and is constructed for each wavefunction. The multiwavelet approximation of each wavefunction has its own adaptive resolution to the desired precision.

3. Algorithm

In [7, 5], we described algorithms for solving Schrödinger equation without the spin-orbit term. We proceeded in two steps. First, we represented the approximate wave functions and the Hamiltonian operator in the multiwavelet basis in a large enough domain so that the tails of the wavefunctions are 0, and diagonalized the eigensystem using LAPACK’s Hermitian eigensolver to obtain estimates for the eigenvalues and orthogonal eigenfunctions. This is fast for a small number of eigenvalues and eigenvectors. Once the orthogonal eigenvectors have been obtained, we refined the approximation for the eigenvectors, constructed and applied the bound-state Helmholtz Green’s functions for each estimated eigenvalues and iteratively solved the Lippman-Schwinger equation associated to the Schrödinger equation.

Our algorithm based on direct diagonalization with fixed-point iteration is given below. If $V_{SO}$ is not included, the Green’s function iteration summarized above [7] converges quickly to high accuracy.

Our algorithm for the solving the spin-orbit Hamiltonian is

- Initialize all guess wave-functions $\phi_i^0$ for all $i$, $n = 0$
- Loop on $n$ until converged
  1. Form matrices $\mathbf{H} = \langle \phi_i^n, \mathbf{H} \phi_j^n \rangle$, $\mathbf{S} = \langle \phi_i^n, \phi_j^n \rangle$
  2. Solve the orthogonal generalized eigenproblem for the eigenpair $(E_i^n, \phi_i^n)$
  3. Refine the multiwavelt expansion of $\phi_i^n$
  4. Construct the LSR approximation of the Green’s function $G_i$
  5. Apply a fixed-point convolution iteration\(^1\), $\phi_i^{n+1} = -G_i \ast (VI + V_{SO})\phi_i^n$
  6. Compute the relative norm of the change in eigenvectors $\phi_i$
  7. If the relative norm is less than norm, label $\phi_i$ converged
  8. Update counter, $n = n + 1$

where $G_i(r) = e^{-k_ir}/r$, $r = \sqrt{x^2 + y^2 + z^2}$, $k_i = \sqrt{-2m/\hbar^2} E_i$. In practice one can show that if the norm of $G \ast V_{SO} \phi$ is small relative to $G \ast V \phi$ then the iteration converges. Formal proof will be presented elsewhere.

4. Test problem

The above algorithm has been applied to solve the Schrödinger equation for a non-spherically symmetric potential from nuclear density function theory using the MADNESS code. The potential $V$ is the two-center cosh potential

$$V(x, y, z) = \frac{V_1}{1 + e^{-R_1/a_1} \cosh(\frac{r_+/a_1}{a_1})} + \frac{V_2}{1 + e^{-R_2/a_2} \cosh(\frac{r_-/a_2}{a_2})}$$

\(^1\) The symbol $\ast$ denotes the convolution operation.
with \( V_1 = V_2 = -50 \) MeV; \( a_1 = a_2 = 1.0 \) fm; \( R_1 = R_2 = 2.0 \) fm. The potential wells are at \( r_- = (0, 0, -\zeta) \) and \( r_+ = (0, 0, \zeta) \) with \( \zeta = 7.5 \) fm. The spin-orbit term is described above as \( V_{SO} \) and is also given by Eq. (22) in [9].

A comparison of the results from basis expansions using the harmonic oscillator basis and also the spline basis are included for comparison in Figure 1. The computation with the spline basis uses a 2-D tensor product expansion with up to degree 11 elements in each dimension. For the calculation using the harmonic oscillator basis, a 3-D tensor product of up to 25 shells and with degree up to 22 in each dimension is used. Due to memory usage both of these boxes were only able to use a domain \([-40., 40.]\), in fermies, in each spatial direction. The MRA computation uses a tensor product of degrees 0 to degree 7 multiwavelets in each dimension. The precision of the multiwavelet calculation is \( 1e^{-5} \) using a domain \([-120., 120.]^3 \). Some of our results are reported in [9].

Three dimensional plots of the absolute value of the real part of the 6-th and the 8-th wavefunctions, \( \log(|u|) \), are displayed in Figure 2. Various isosurfaces of the wavefunctions show the complicated structures as well as the symmetries of the wavefunctions.

### 5. Acknowledgements

This work was supported by the Scientific Discovery through Advanced Computing (SciDAC) program of the U.S. Department of Energy, Office of Science, the Division of Basic Energy Sciences, and the Office of Advanced Scientific Computing Research, Program in Applied Mathematics and through the SciDAC Scientific Application Pilot Program under contract number DE-AC05-00OR22725 with UT-Battelle, LLC (Oak Ridge National Laboratory). It is also supported under contracts DE-FG02-96ER40963 (University of Tennessee), DE-FG05-87ER40361 (Joint Institute for Heavy Ion Research), and DE-FC02-07ER41457 with UNEDF SciDAC Collaboration. Computational resources were provided by the National Center for Computational Sciences at Oak Ridge and the National Energy Research Scientific Computing Facility.

### References

[1] B. Alpert. A class of bases in \( L^2 \) for the sparse representation of integral operators. *SIAM J. Math. Anal*, 24(1):246–262, 1993.

[2] E. Anderson, Z. Bai, C. Bischof, S. Blackford, J. Demmel, J. Du Croz, A. Greenbaum, S. Hammarling,
Figure 2. The logarithm of the absolute value of the real part of the wavefunctions corresponding to eigenvalue number 6 (labeled log(u13)) and number 8 (labeled log(u17)) with various isosurfaces are plotted with domain $[-20, 20]^3$. 
A. McKenney, and D. Sorenson, editors. *LAPACK User’s Guide, Third Edition*. SIAM, Philadelphia, PA, 1999.

[3] G. Beylkin, R. Cramer, G.I. Fann, and R.J. Harrison. Multiresolution separated representations of singular and weakly singular operators. *Appl. Comput. Harmon. Anal.*, 23(2):235–253, 2007.

[4] Ernest R. Davidson. Super-matrix methods. *Comp. Phys. Comm.*, 53:49–60, 1989.

[5] G.I. Fann, G. Beylkin, R.J. Harrison, and K. Jordan. Singular operators in multiwavelet bases. *IBM Journal of Research and Development*, 48(2):161–171, March 2004.

[6] G. Golub and C. Van Loan. *Matrix Computations*. Johns Hopkins University Press, 3rd edition, 1996.

[7] R.J. Harrison, G.I. Fann, T. Yanai, and G. Beylkin. Multiresolution quantum chemistry in multiwavelet bases. In P.M.A. Sloot et. al., editor, *Lecture Notes in Computer Science. Computational Science-ICCS 2003*, volume 2660, pages 103–110. Springer, 2003.

[8] R.J. Harrison, G.I. Fann, T. Yanai, Z. Gan, and G. Beylkin. Multiresolution quantum chemistry: basic theory and initial applications. *J. Chem. Phys.*, 121(23):11587–11598, 2004.

[9] J.C. Pei, M.V. Stoitsov, G.I. Fann, W. Nazarewicz, N. Schunck, and F.R. Xu. Deformed coordinate-space Hartree-Fock-Bogoliubov approach to weakly bound nuclei and large deformations. *Physics Review C*, 78, 064306, 2008.

[10] T. Yanai, G.I. Fann, Z. Gan, R.J. Harrison, and G. Beylkin. Multiresolution quantum chemistry: Analytic derivatives for Hartree-Fock and density functional theory. *J. Chem. Phys.*, 121(7):2866–2876, 2004.