Multiresolution Quantum Chemistry in Multiwavelet Bases

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Abstract. Multiresolution analysis in multiwavelet bases is being investigated as an alternative computational framework for molecular electronic structure calculations. The features that make it attractive include an orthonormal basis, fast algorithms with guaranteed precision and sparse representations of many operators (e.g., Green functions). In this paper, we discuss the multiresolution formulation of quantum chem-

- a fully orthonormal basis with high-order convergence even in the presence of singularities,
- an algorithm for adaptive refinement,
- sparse representations of many operators including the Hamiltonian and Green functions, and
- fast algorithms with guaranteed precision for many common operations.

The high-order, orthonormal basis with adaptive refinement enables robust high-precision computation. The separation of length scales implicit in the multiresolution formulation provides sparse representation of operators which enables fast computation. Although the orthonormal multiwavelet basis may be used in standard matrix (i.e., Hamiltonian) formulations of quantum problems, it is often much more effective to reformulate the problem as an integral equation.

In the following, we use the Poisson equation to introduce the essential details of multiresolution in multiwavelet bases and how they result in fast algorithms. Subsequently, we discuss an essential component for efficient computation in many dimensions, which is accurate separated representations of integral operators. This is done in the context of an integral formulation of density functional theory (DFT). Finally, we briefly describe our prototype implementation.

2 Sparse Representations and Fast Algorithms

Much of our discussion is, for simplicity, in one dimension, but the generalization to higher dimensions is straightforward, except where otherwise noted.

We map the problem to the unit interval. This is recursively divided by two, so that on each level $n = 0, 1, 2, \ldots$ there are 2^n boxes. In each box, we define basis functions that are the first k normalized Legendre polynomials inside the box and are zero outside. Smooth functions may be represented with an error $O(2^{-nk})$. By construction, the basis on a level is orthonormal and the functions associated with different boxes do not overlap each other. This last property of disjoint support is the most important advantage of multiwavelet bases. If boundaries or discontinuities are located at the nodes, high-order convergence may be maintained.

The basis at a given level of refinement is of dimension $k2^n$

error is accomplished by discarding small wavelet coefficients [5]. We presently use Alpert's definition of the multiwavelet basis [7].

Since V_n^k is the space of polynomials on level n, the first k moments vanish for functions in W_n^k (since they are by construction orthogonal to V_n^k). This property gives rise to sparse representations of smooth functions and operators. We use the Poisson equation in three dimensions

$$^2u = -4\pi\rho \tag{4}$$

with free-space boundary conditions ($u(\quad) = u'(\quad) = 0$) as an example of how this enables us to replace iterative solution of differential equations with fast application of integral operators.

The matrix representation of the Laplacian in either the multiwavelet basis or standard discretizations is badly conditioned. Moreover, the largest eigenvalues are associated with the highest frequencies. This leads to the requirement of good preconditioners for the efficient iterative solution of differential equations. However, the Green's function for the Poisson equation is known and we may immediately write the solution as

$$u(r) = \int \frac{\rho(s)}{r - s}\, ds. \tag{5}$$

That the multiwavelet representation of this integral operator is sparse can be readily seen from the multipole expansion of $1/r$

3 Integral Formulation of the Schrödinger Equation

The familiar Hamiltonian formulation of the Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 + V\right)\psi = E\psi \tag{7}$$

may be rewritten as an integral equation

$$\psi = -2\left(\nabla^2 - 2E\right)^{-1} V\psi \tag{8}$$

where the inverse of the differential operator denotes application of the corresponding Green function. For bound states, the Green function is that of bound-state Helmholtz equation, which, in three dimensions, is given by

$$G(r, s, E) = \frac{e^{-\sqrt{-2E}\,|r-s|}}{4\pi\,|r-s|}. \tag{9}$$

This kernel is amenable to fast computation in the multiwavelet basis just as described for the Poisson kernel. Moreover, straightforward iteration of (8) will converge to the ground state, whereas an iterative, preconditioned eigensolver must be used to solve the differential form. For DFT models without Hartree-Fock exchange, the form of the integral operator includes the expected asymptotic exponential decay. To extract multiple roots from the integral equation we use deflation which is discussed elsewhere [8].

4 Practical Application of Integral Operators in Three Dimensions

Above, the application of integral operators has been informally demonstrated to be efficient, in the sense of scaling linearly with the number of boxes with significant coefficients. However, practical computation also requires a small prefactor. In three dimensions, the basis within each box on the locally finest level will be

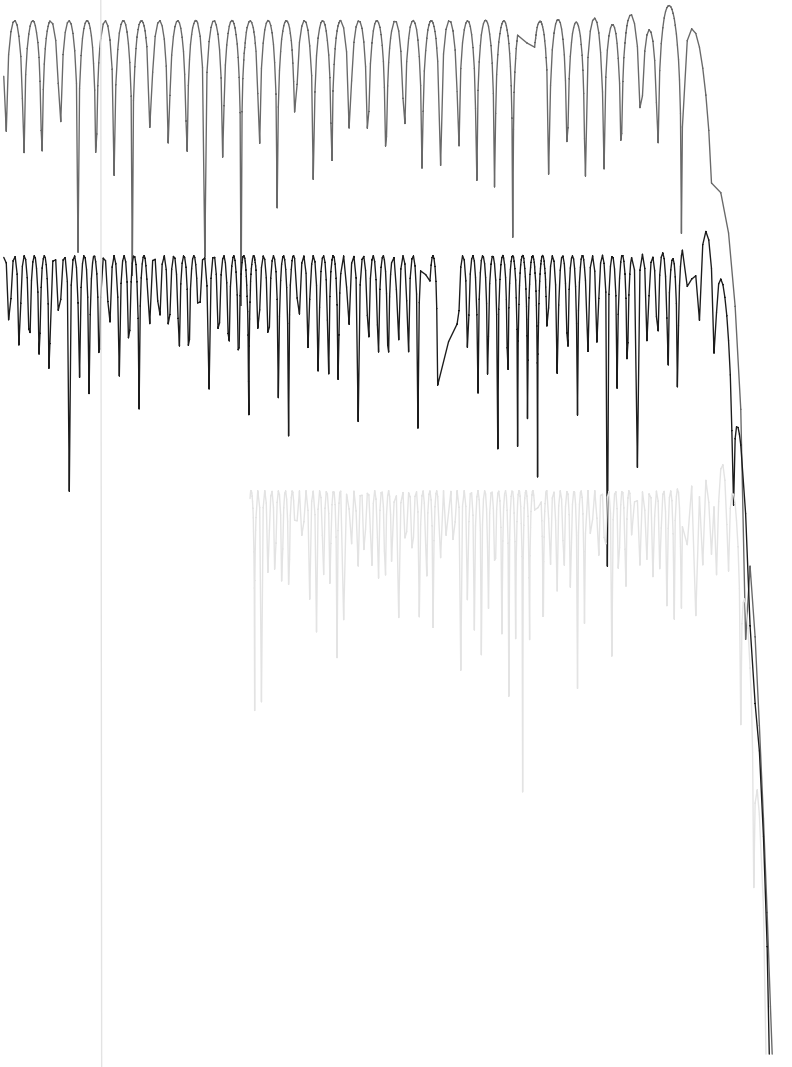
where l and l' label the result and source boxes, and $\varphi_i^{nl}(x)$ is the i'th Legendre polynomial in box l on level n. If there existed a separated representation of the kernel that is accurate to our desired precision

$$K($$

$$s_{lo} = \log(4T/\mu^2)/2 \tag{16}$$

$$1/h = .2 + 0.47 \log_{10} \tag{17}$$

where the range of the quadrature is $[s_{lo}, s_{hi}]$, the expansion has a relative precision of over the range $[r_{lo}, 1]$, and h is the spacing of the quadrature points. The parameter T is empirically determined to be 5, 10, 14, 18, and 24, respectively for accuracies 1e-2, 1e-4, 1e-6, 1e-8, and 1e-10. However, because of the super-exponential decay, the number of quadrature points is only weakly dependent upon T



The orthonormal basis enables all of the familiar results of quantum theory to be used without change, though the greatest benefit is obtained by reformulating the entire solution scheme to take advantage of the properties of the basis. In particular, the sparse representation of many integral operators, including many physically significant Green functions, enables new approaches. Additional techniques are necessary for scattering states for which the corresponding Green functions do not become smooth at long range. Compact separated representations are important for efficient computation in higher dimensions, and may also be of utility in conventional Gaussian-based methods. Finally, although our current implementation uses orbitals, so cannot attain full linear scaling, it is well established [11,12,13] that a density-matrix approach in a wavelet basis will achieve linear scaling while maintaining a guarantee of arbitrary, finite precision.

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