

**Scientific Application Prototype Project  
Fundamental Algorithms for Advanced Applications in  
Science and Technology-*Low Separation Rank Approximations for  
Computational Chemistry***

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### Summary

*We've derived and developed a new fast  $O(N)$  algorithm based on multiresolution and separated representations of singular operators in three and higher dimensions. These representations have been applied to fast, scalable and highly accurate computational chemistry computations. Fundamental mathematical techniques were developed for approximating separated form of functions and operators, up to arbitrary but finite precision, that is compatible with multiwavelet representation of functions and operators.*

Singular operators are ubiquitous in problems of physics. The Hilbert transform and the Coulomb kernel are just some of the important examples with wide ranges of applications in computational chemistry, computational electromagnetics, fusion and fluid dynamics.

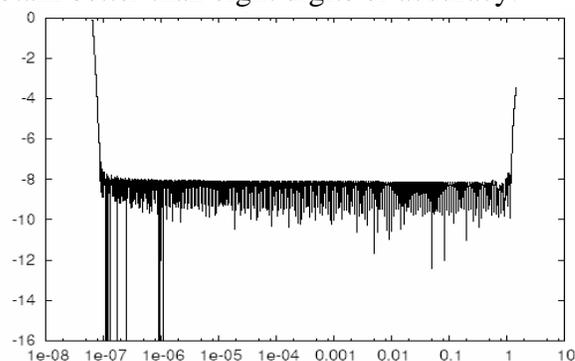
Theoretically, it has been clear for some time that a multiresolution representation of homogeneous operators should lead to useful numerical algorithms. However, the straightforward transition from one spatial dimension to three dimensions and beyond yields algorithms which are too time consuming for practical high precision applications.

We've recently develop a multiresolution approach using a new separable representation of functions in conjunction with multiwavelet bases. For example, we can approximate the six singular Green's

functions for projector on the divergence-free functions with exponentials

$$\left| p_{ij}(r) - \sum_{m=1}^M w_m e^{-p_m \|r\|^2} \right| \leq \frac{\epsilon}{\|r\|^2}.$$

For the domain  $[10^{-7}, 1]$  with  $M=110$ , we obtain better than eight digits of accuracy.

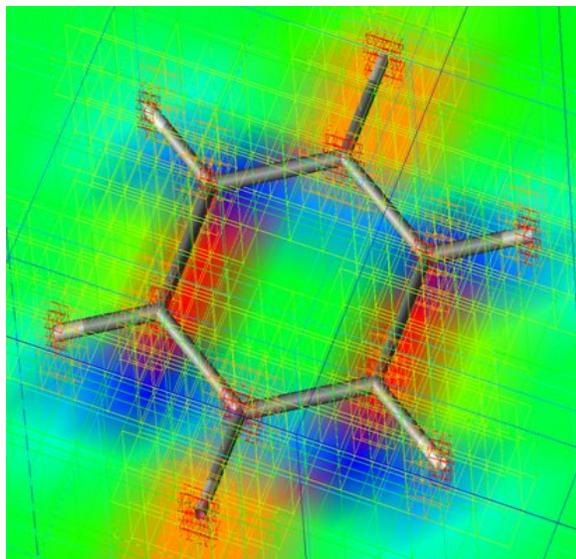


This approach was a magnitude faster and used far less memory than the generic wavelet approach.

In particular, we constructed and used separable representations for the Green's function for the Poisson and the bound-state

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Helmholtz equations in computational chemistry. These constructions, combined with adaptive multi-resolution multiwavelet representations and a numerical regularization procedure, make our approach practical and fast in three dimensions. We are investigating its application in six dimensions.



*Figure 1. Adaptive grids are automatically generated for molecular orbital simulations. An orbital of benzene and a slice through that orbital are shown.*

These new techniques have been applied by Robert Harrison and his group (funded by SciDAC BES) to perform highly accurate electronic structures computations. A prototype software implementation has been developed for parallel computers for density functional theory and Hartree-Fock energies, analytic derivatives with respect to atomic positions, and linear response theory for excited states. This code has been applied to atoms as heavy as barium and many molecules comprising first, second and third elements. Each simulation has been able to duplicate the most accurate result in the literature. An example of the simulation for the methane molecule is displayed on Figure 1.

The successful demonstration of a basis free one-electron method based on multi-resolution analysis is a precursor to direct numerical solution of many electron problems. Numerical solutions of two and many electron problems will require solutions of six and higher dimensional Schrödinger equation. This a significant challenge since most algorithms are formulated for only up to three dimensions. It is for these higher dimensional problems that we anticipate the benefits of our approach.

This is a significant application in three and higher dimensions of multiwavelet bases and low separation rank methods for partial differential and integro-differential equations. The close collaboration of mathematicians and computational chemists has greatly accelerated the application of new mathematics and numerical methods to practical applications.

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