

2025年 1 月 16 日

機能材料 工学専攻	学籍番号	D053708	指導 教員	関野 秀男
申請者 氏名	加藤 哲也			栗田 典之

## 論文要旨 (博士)

論文題目	多重解像度多重ウェーブレット基底の量子化学計算への応用
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(要旨 1,200 字程度)

量子力学に基づく計算は、基礎理論は20世紀初頭に整ったが、当時は現実的に不可能な量の計算が必要であった。電子コンピュータの発明以降は応用的な計算が可能となり、化学の分野でも、Schrödinger方程式の平均場近似によるHartree-Fock方程式を行列方程式として表した、Roothaan方程式を基盤として、Hartree-Fock, post-Hartree-Fockの各手法、そして密度汎関数理論とKohn-Sham方程式による各種の解法が実装されてきた。基底状態の電子状態を解くだけにとどまらず、エネルギーの核座標微分の計算により、第一原理的な分子構造計算が可能となり、これは特に、理論の専門家ではない、実験家達にもカジュアルに用いられるほど普及した。

しかしながら、伝統的なLCAO型の基底では、大規模系の計算で必要となる巨大な固有値計算を実行することが、現代的な超並列計算機を用いても簡単ではないことや、特に応答関数を必要とする計算で物性の定量的な評価が難しいことが知られるようになってきた。

MADNESSは、離散ウェーブレット変換を基礎にした3次元直交空間上の基底である多重解像度多重ウェーブレット(Multi-Resolution Multi-Wavelet; MRMW)基底の技術をベースに、超並列計算を前提に設計された科学計算ライブラリである。MADNESSはC++で記述され、アプリケーション開発者はほとんど並列化を意識することなく、数式に近い形でアルゴリズムを記述できる。MADNESS上では基本的なHartree-Fock, 及びLDA(Local Density Approximation)によるDFT計算が実装されている。

本研究では、既存の量子化学計算に利用される技術を、MADNESSを利用して動作するプログラムへ実装することにより、既存技術のLCAO依存性を明らかにし、3次元直交基底上での応用可能性について調べた。

第1に、擬ポテンシャル法の一つであるModel Core Potentialを実装した。擬ポテンシャル法は内殻電子群を局所ポテンシャルと非局所ポテンシャルで近似し、変分空間を削減して、計算負荷を軽減する手法であり、LCAO基底では広く用いられている。本研究では新たなパラメータフィッティング手法を提案し、その精度を確かめた。

第2に、CPHF/KS(Coupled Perturbed Hartree-Fock/Kohn-Sham)法を実装し、水素分子共鳴領域の周波数依存動的分極率について、LCAO基底との比較を行った。水素分子のような最も単純な分子であっても、LCAOでは精度を上げるために恣意的な基底選択を行う必要があるが、MRMW基底ではそのようなことはないことが確認できた。

これらの実装、計算を通じ、LCAO基底で用いられた種々の手法の直交空間上の基底への移植性と、各々の基底の特徴について考察した。

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Department	Functional Materials Engineering	ID	D053708
Name	KATO Tetsuya		

Supervisor	SEKINO Hideo KURITA Noriyuki
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### A b s t r a c t

Title	Application of Multi-resolution Multi-wavelet for the quantum chemistry
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(800 words)

In early 20<sup>th</sup> century, basic theories are prepared for quantum dynamics calculation. However, it was impossible then to execute the calculation because it requires large amount of calculation. After invention of electronic computer, it becomes possible even for applicative purpose.

In chemistry, many methods are implemented such as Hartree-Fock, post-Hartree-Fock methods, the Kohn-Sham equation by Density Functional Theory based on the Roothaan equations that represent the Hartree-Fock equation which approximates the Schrödinger equation with mean field approximation as a matrix form. It is not only for electronic state of ground state but also *ab initio* geometry optimization using energy gradient by nuclear coordinates that becomes common to be used by experimentalists who are not a specialist of theory.

Nevertheless, using traditional LCAO (Linear Combination of Atomic Orbitals) type basis functions, it is difficult to solve large eigenvalue problem needed for a calculation of large molecular system or to estimate response properties quantitatively.

MADNESS is a scientific calculation library that targets massively parallel computing and using MRMW (Multi-Resolution Multi-Wavelet) basis that is constructed based on Discrete Wavelet Transform technique. Just enough number of MRMW basis functions are spread over 3D bounding box to represent target function. It is guaranteed that a function represented with the MRMW basis is close to the target function within a given threshold.

Basic operations for 3D real/complex-valued functions are implemented and Hartree-Fock and DFT using LDA (Local Density Approximation) functionalities are also implemented. During its execution, MRMW basis coefficients are transformed, and MRMW basis functions are deleted or spawned as necessary by function operations automatically. MRMW basis functions are spawned depending not on nuclear geometries but on the shape of target function.

MADNESS solves the SCF problem using a Green's function for the Bound State Helmholtz equation. Molecular orbitals are solved as a set of orbitals under Hartree-Fock/DFT potentials generated by other electrons one by one. Therefore, there are no need to solve eigenvalue problem. Orbital updating procedure spends only  $O(N)$ . If using LDA-DFT, all of calculations are done in  $O(N)$ . To say fairly, transformation of MRMW coefficients tree consumes  $O(\log M)$  which comes from target function complexity. Total calculation cost in order is still  $O(N \log M) < O(N^2) \ll O(N^4)$ . Multi-wavelet has shallower tree than Single-wavelet, so  $M$  is usually small.

MADNESS is written in C++ so that developers write applications like mathematical formulas, without need to concern about parallel techniques over MADNESS libraries.

In this study, we implement existing techniques used for calculations of traditional quantum chemistry to MADNESS to show capabilities to apply them to 3D orthogonal basis despite of LCAO dependencies of the techniques.

First, we implement a Model Core Potential which is one of pseudo-potentials. The pseudo-potential is a method commonly used in LCAO basis to reduce amount of calculation by replacing inner shell electrons with local and non-local potentials. It is also useful to calculate very heavy atoms which need relativistic treatment. Inner shell electrons of heavy atoms have very high velocity near the light speed but valence electrons move slowly. Hence we can calculate heavy atoms with non-relativistic equations if inner shell electrons are replaced to potentials including the relativistic effects. We find that MCP depends on basis set strongly and its consistency is easily broken by adding basis function even in LCAO fashion. We propose new method to fit potential parameters to make MCP consistent in MRMW and confirm its accuracy.

Second, we implement a CPHF/KS (Coupled Perturbed Hartree-Fock/Kohn-Sham) method to MADNESS and compare results against LCAO basis using dynamic polarizability depends on frequency of the external field with resonance region of  $H_2$ . Quantitative estimation of dynamic polarizability  $\alpha$  in resonance region is hard because  $\alpha$  can be represented by a equation with denominator with a different between external field frequency minus excitation energy. Therefore  $\alpha$  quickly diverges for the frequency close to excitation energy. It is known that in LCAO basis, dynamic polarizability estimation requires diffuse type function in basis set. MRMW basis can represent diffuse type function and a function far from nuclei. LCAO basis are designed for representing ground state orbitals. Response functions which are needed for calculate  $\alpha$  can have different characteristics against ground state orbitals.

We confirm that it is difficult to select a basis set automatically even with the simplest molecule  $H_2$  to calculate accurately using LCAO. In contrast, it is done automatically with the MRMW basis. MRMW always reproduce target function with guaranteed accuracy even if we don't have any information of target function in advance. LCAO basis sets, or any basis function sets which have specific function type, needs information of target function shape.

We discuss interchangeabilities of methods developed in LCAO basis with the MRMW basis set and characteristics of both basis sets through these implementations and calculations.