

Basis set limit molecular properties using multiwavelets



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Introduction

We present the implementation of **MRChem**, a real-space all-electron self-consistent field (SCF) program that is based on multiresolution multiwavelet (MRMW) bases. MRMWs provide strict error control and automatic grid generation, and unlike the traditional Gaussian type (GTO) bases they do not require careful preoptimization in order to get reliable results on different molecular properties. The method comes with a large prefactor, but the inherent low scaling combined with the possibility of massively parallel algorithms will probably make MRMWs competitive with GTOs in the future. We compute molecular properties through linear response, and demonstrate the accuracy of the method by computing a set of important electric and magnetic properties.

The multiresolution multiwavelet (MRMW) basis

The MRMW basis consists of two types of polynomials: scaling and wavelets functions. A **scaling** projection at scale N gives an approximation with polynomial grid cells of resolution 2^{-N}

$$f(x) \approx f^N(x) \quad (1)$$

The **wavelet** projections df^n are defined as the *difference* between two consecutive scaling projections

$$df^n(x) = f^{n+1}(x) - f^n(x) \quad (2)$$

By recursive application we get an alternative (and sparse) **multiresolution** approximation f^N

$$f(x) \approx f^N(x) = f^0(x) + \sum_{n=0}^{N-1} df^n(x) \quad (3)$$

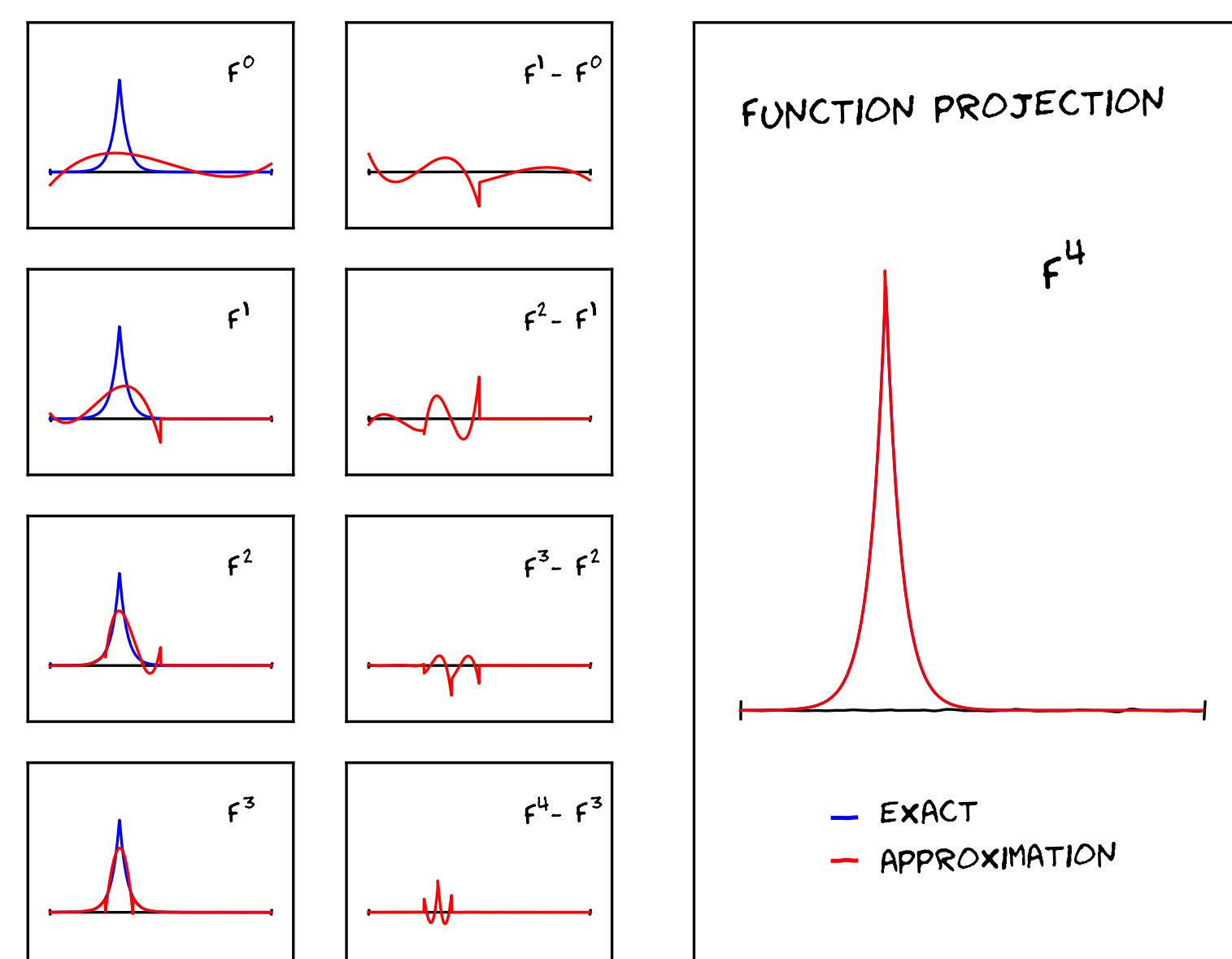


Figure 1: Scaling and wavelet projections of an s-type orbital.

Integral formulation self-consistent field

The MRMW basis allows for efficient and linear-scaling application of integral operators in the form

$$\hat{G}[f](r) = \int G(r-r') [f(r')] dr' \quad (4)$$

including the Bound-State Helmholtz (BSH) operator with integral convolution kernel

$$G(r-r') = \frac{e^{-\mu|r-r'|}}{4\pi|r-r'|} \quad (5)$$

The parallel performance of the the Poisson operator ($\mu = 0$) has been demonstrated for electrostatic potentials on large molecular systems[2].

The Kohn-Sham/Hartree-Fock equations

$$[\hat{T} + \hat{V}] \varphi_i = \epsilon_i \varphi_i \quad (6)$$

is written in integral form using the BSH operator, which is the inverse of the shifted kinetic operator

$$2\hat{G}_i = [\hat{T} - \epsilon_i]^{-1} \quad (7)$$

The equations can be solved iteratively[3]

$$\varphi_i^{n+1} = -2\hat{G}_i [\hat{V}^n \varphi_i^n] \quad (8)$$

up to any finite precision relative to the basis set limit.

Solving the SCF problem of the perturbed system up to first order yields a Sternheimer[4] (coupled perturbed HF/KS) equation for the perturbed orbitals x_i and y_i . Using the projector onto the occupied space

$$\hat{\rho}^{(0)} = \sum_i |\varphi_i\rangle \langle \varphi_i| \quad (12)$$

and the BSH operator of the unperturbed orbital energy ϵ_i shifted by the perturbing frequency ω

$$2\hat{G}_i^{(\pm)} = [\hat{T} - (\epsilon_i \pm \omega)]^{-1} \quad (13)$$

we arrive at the coupled linear response equations[5, 6]

The final working equations for dynamic linear response

$$x_i = -2\hat{G}_i^{(+)} \left[\hat{V}^{(0)} x_i + (1 - \hat{\rho}^{(0)}) (\hat{h}^{(1)} + \hat{V}^{(1)}) \varphi_i \right] \quad (14)$$

$$y_i = -2\hat{G}_i^{(-)} \left[\hat{V}^{(0)} y_i + (1 - \hat{\rho}^{(0)}) (\hat{h}^{(1)} + \hat{V}^{(1)})^\dagger \varphi_i \right] \quad (15)$$

The response equations are solved using the same machinery as for the ground-state SCF problem, and fully numerical representations of the response functions can be obtained to high accuracy. The molecular property for a pair of operators $\hat{h}^{(a)}$ and $\hat{h}^{(b)}$ are then obtained as

$$M^{a,b} = \int \hat{h}^{(a)} \hat{\rho}^{(b)} dr \quad (16)$$



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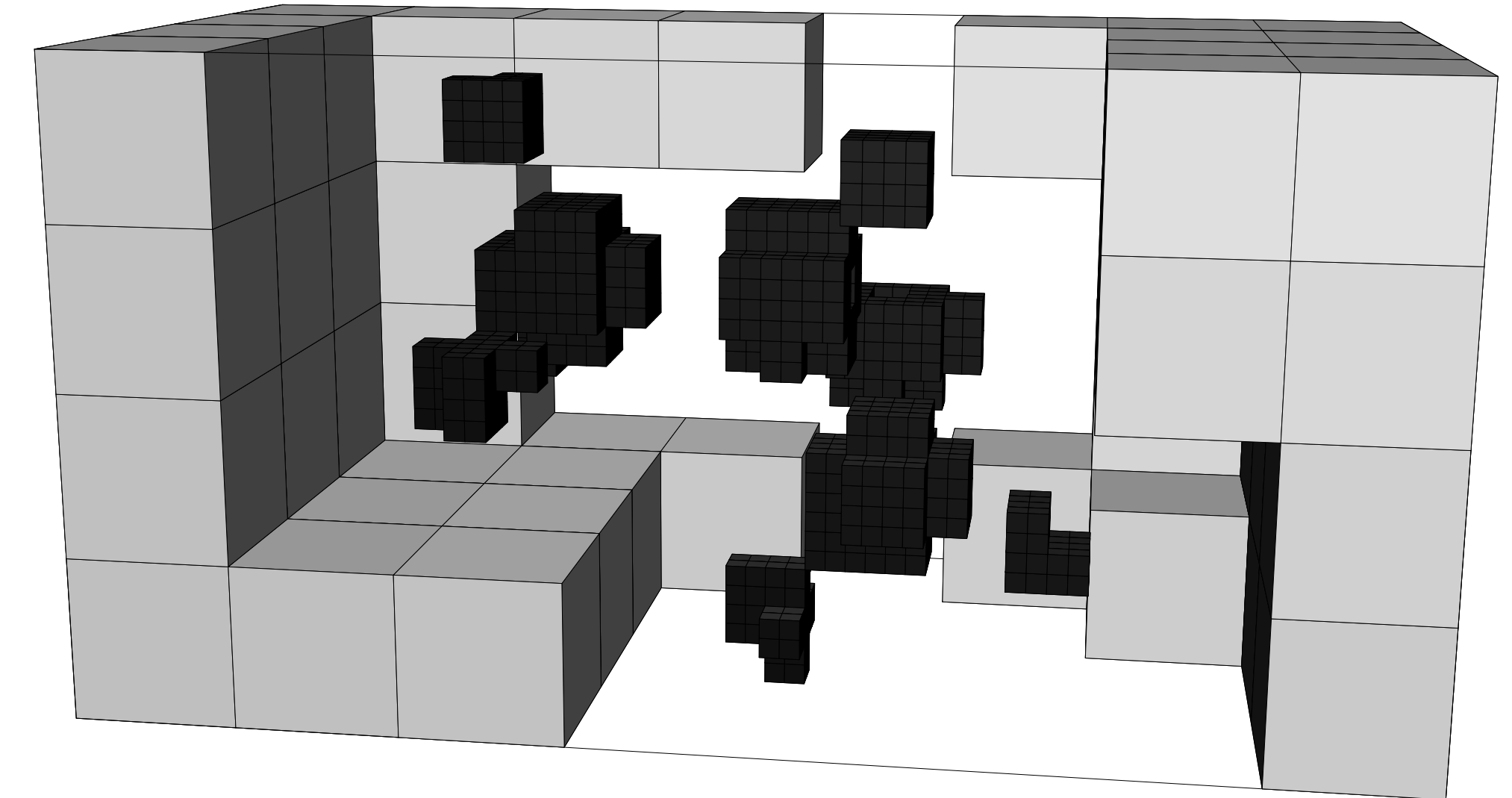
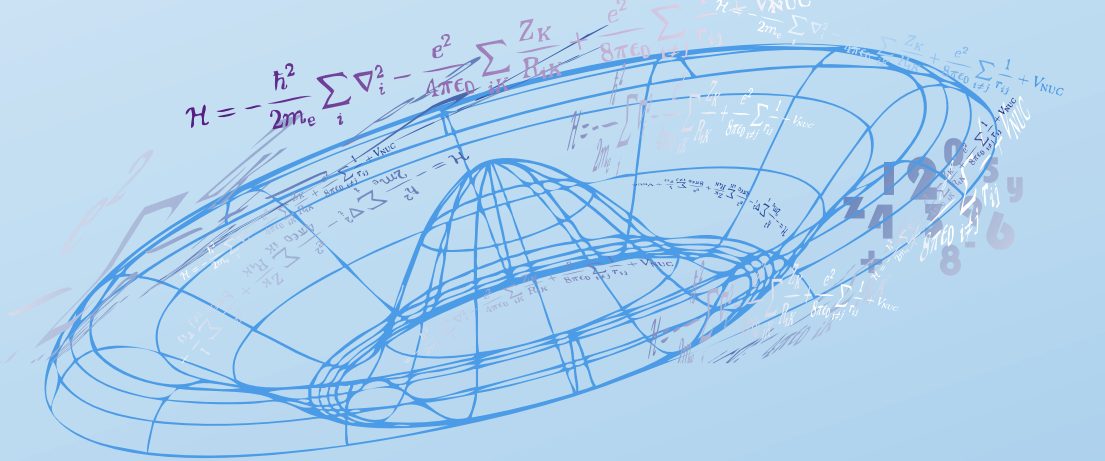


Figure 2: Adaptive grid for electron density of methyloxirane.

Results

Table 1: Total energies at Hartree-Fock and LDA (SVWN5) levels of theory. GTO calculations by Dalton[1]. In the MRChem calculations, the orbitals are converged to the given threshold (the overall accuracy in the calculations is set two orders of magnitude higher in order to get quadratic convergence in the energy).

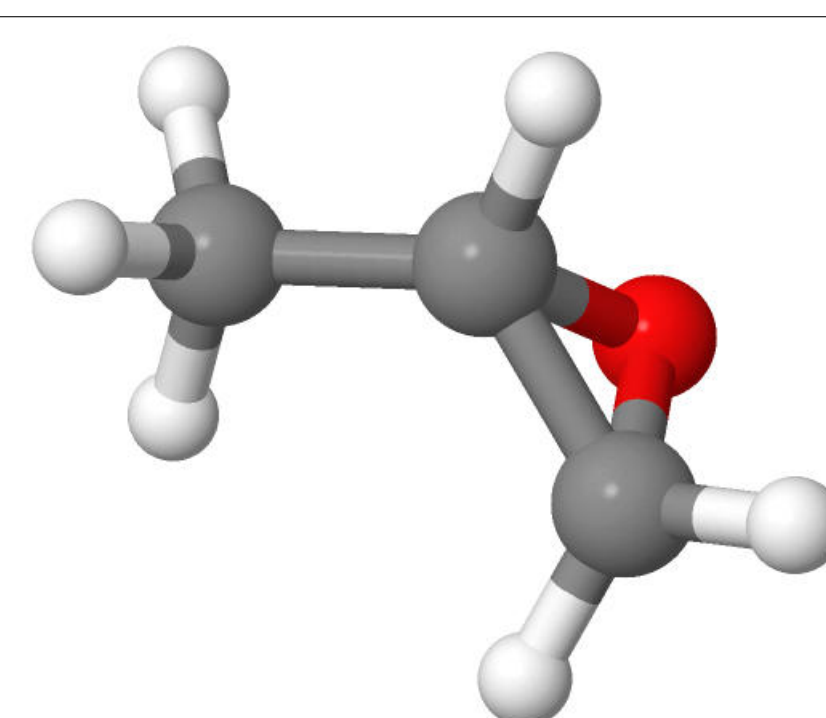
	Energy (a.u.)		CH ₃ CHCH ₂ O
	Hartree-Fock	LDA	
MRChem 10 ⁻²	-192.0425	-191.5975	
MRChem 10 ⁻³	-192.0002	-191.5622	
MRChem 10 ⁻⁴	-192.0000	-191.5619	
aug-cc-pVQZ	-191.9968	-191.5563	
aug-cc-pVDZ	-191.9357	-191.4817	
cc-pVQZ	-191.9960	-191.5549	
cc-pVDZ	-191.9232	-191.4622	

Figure 3: Methyloxirane molecule.

Table 2: Polarizability and optical rotation calculated at LDA (SVWN5) level of theory. Dynamic response at the sodium D line (589.3 nm) wavelength. GTO calculations using gauge-including atomic orbitals (GIAO) by Dalton[1].

LDA	Polarizability (a.u.)		Optical rotation (a.u.)	
	Static	Dynamic	β	α
MRChem 10 ⁻²	44.0764	45.2747	0.009376	6.2440
MRChem 10 ⁻³	44.0939	45.2907	0.010427	6.9439
MRChem 10 ⁻⁴	44.0935	45.2903	0.010556	7.0298
aug-cc-pVQZ	44.1326	45.3380	0.009861	6.5669
aug-cc-pVDZ	44.0050	45.2025	0.000776	0.5170
cc-pVQZ	42.3602	43.4064	0.001239	0.8249
cc-pVDZ	36.5586	37.3993	-0.065879	-43.8711

Table 3: Magnetic properties calculated at Hartree-Fock level of theory. GTO calculations by Dalton[1] with gauge-including atomic orbitals (GIAO). Magnetizabilities are also computed without GIAOs using different origins to test the origin dependence.

Hartree-Fock	Magnetizability (a.u.)			NMR shielding (ppm)		
	GIAO	(0, 0, 0)	(5, 5, 5)	ξ^{dia}	ξ^{para}	ξ^{tot}
MRChem 10 ⁻²		-9.5497	-9.9222	446.7869	-96.6166	350.1703
MRChem 10 ⁻³		-9.4730	-9.4363	447.3444	-91.7855	355.5589
MRChem 10 ⁻⁴		-9.4758	-9.4795	447.3089	-90.9386	356.3704
aug-cc-pVQZ	-9.4736	-10.5253	-26.0533	447.7508	-90.6691	357.0817
aug-cc-pVDZ	-9.5369	-15.4438	-101.6430	451.0119	-88.5778	362.4341
cc-pVQZ	-9.4681	-10.8019	-29.2395	447.7833	-89.6304	358.1529
cc-pVDZ	-9.4924	-19.0342	-140.0203	451.6103	-87.4153	364.1950

Conclusions

We have shown that by making use of the properties of the MRMW basis we have strict control of the basis set error, and we are able to reach the basis set limit (within a predefined accuracy) for several linear response properties. The method does not rely on gauge including or preoptimized basis set in order to give high quality results.

The calculations are at present still demanding, both in terms of memory and CPU time, and are competitive to GTOs only when high accuracy is required.

References

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