Dirac-Fock calculations on molecules in an adaptive multiwavelet basis

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ABSTRACT

We report the first fully numerical approach for relativistic quantum chemical calculations applicable to molecules. The approach uses an adaptive basis of multiwavelet functions to solve the full four-component Dirac-Coulomb equation to a user-specified accuracy. The accuracy of the code is demonstrated by comparison with ground state energy calculations of atoms performed in GRASP, and the applicability to molecules is shown via ground state calculations of some simple molecules, including water analogs up to H_2Po. In the case of molecules, comparison is made with Gaussian basis set calculations in DIRAC.

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I. INTRODUCTION

Quantum chemistry, in principle, enables accurate calculations of molecular properties, but for higher accuracy calculations, especially those involving heavier atoms, one must take into account the effects of special relativity.[1] There has been success in adapting existing basis-set methods to handle the effects of special relativity, but these come with the same weaknesses of nonrelativistic basis-set calculations, i.e., poor scaling with respect to number of basis functions, and the large number of linear dependencies when calculating with large basis sets.[2] Additionally, basis sets for relativistic calculations must be chosen and contracted even more carefully to maintain the correct relation between the large and small components to avoid variational collapse.[3] Fully numerical codes exist, but only for atoms[4] or small molecules of high symmetry.[5–7] MADNESS[8] provides the first fully numerical relativistic code that can be applied to general molecules, and this paper details the implementation and initial results. In Sec. I A, we briefly review the Dirac equation and the integral equation approach. A brief description of the multiwavelet basis used by MADNESS is given in Sec. I B. In Sec. II, we give the details of our calculations, and we present results in Sec. III. In Sec. IV, we make some concluding remarks and discuss future directions.

A. Dirac-Fock

The relativistic Dirac-Fock equation is given by

$$(h_d + V + J - K)\varphi_i = \varepsilon_i \varphi_i, \tag{1}$$

$$h_d = c\,\boldsymbol{\alpha} \cdot \mathbf{p} + \beta m c^2, \tag{2}$$

$$J\varphi_j = \varphi_j(\mathbf{r}) \sum_i \int \frac{\varphi_i^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}', \tag{3}$$

$$K\varphi_j = \varphi_i(\mathbf{r}') \sum_i \int \frac{\varphi_i^*(\mathbf{r}')\varphi_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \tag{4}$$

Here, $c = 137.0359895$ is the speed of light in atomic units, taken from Ref. 9, m is the rest mass of the electron (unity in atomic units), and $\mathbf{p}$ is the 3-component vector of linear momentum operators $p_i = -i\frac{\partial}{\partial x_i}$. V is the external potential. The matrices α_k and β are given by

$$\alpha_k = \begin{bmatrix} 0 & \sigma_k \\ \sigma_k & 0 \end{bmatrix} \quad \beta = \begin{bmatrix} I_2 & 0 \\ 0 & -I_2 \end{bmatrix},$$

$$\sigma_1 = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix} \quad \sigma_2 = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix} \quad \sigma_3 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix},$$

where I_n is the identity matrix of dimension n. Solutions to Eq. (1) are complex-valued 4-component functions and can describe both electronic (positive energy) and positronic (negative energy) states. Methods exist to transform the Dirac equation such that one must only solve a two-component problem for the electronic states. Good reviews of these methods exist, for example, Refs. 10 and 11. Although it is possible to use MADNESS in the context of a two-component formalism, the computational cost is prohibitive for practical calculations as discussed in Ref. 12. Therefore, in this paper, we concern ourselves only with the full 4-component Hamiltonian.

The adaptive multiwavelet basis (to be described in Sec. I B) in MADNESS is not band-limited, so solving Eq. (1) by forming the equivalent matrix eigenvalue problem in the space of basis functions would amplify high frequency noise in the calculation of the matrix elements. For this reason, the integral equation is solved instead by using the associated Green's function. This method has been successfully applied in the nonrelativistic case,[13] and we extend it to the relativistic case here. Rearranging (1) and application of the matrix Green's function associated with the free-particle Dirac equation gives

$$(h_d - \varepsilon_i)\varphi_i(\mathbf{r}) = (K - J - V)\varphi_i(\mathbf{r}), \tag{5}$$

$$\varphi_i = G_i(\mathbf{r}) * [(K - J - V)\varphi_i(\mathbf{r})]. \tag{6}$$

Above, the $*$ represents convolution of the two operands. G_i is the matrix Green's function for the operator on the left-hand side of Eq. (5), i.e., G_i solves

$$(h_d - \varepsilon_i)G_i(\mathbf{r}) = \delta(\mathbf{r})I_4. \tag{7}$$

Its form, provided with proof in Ref. 14, is

$$G_i(\mathbf{r}) = \frac{1}{2mc^2}[h_d + \varepsilon_i]g_i(\mathbf{r}), \tag{8}$$

$$g_i(\mathbf{r}) = \frac{e^{-\mu_i|\mathbf{r}|}}{4\pi|\mathbf{r}|}, \tag{9}$$

$$\mu_i = \sqrt{\frac{m^2c^4 - \varepsilon_i^2}{mc^2}}. \tag{10}$$

Note that the form of Eqs. (8)–(10) changes if the relativistic Hamiltonian used subtracts the rest energy from the standard expression for the relativistic energy of the electron.

B. Multiwavelets

MADNESS employs an adaptively refined multiwavelet basis to represent functions and operators. A detailed description of the multiwavelet basis can be found in Ref. 15, and a brief summary is given here in one dimension, with the extension to multiple dimensions being straightforward. Functions are initially projected into a basis of scaled and shifted Legendre polynomials ϕ_{il}^n. In one dimension and on the interval (0, 1),

$$\phi_i(x) = \begin{cases} \sqrt{2i+1}\,P_i(2x-1) & x \in (0,1) \\ 0 & \text{else,} \end{cases} \tag{11}$$

$$\phi_{il}^n = 2^{\frac{n}{2}}\phi_i(2^n x - l), \tag{12}$$

where $i = 0, 1, \ldots, k - 1$ ranges over the Legendre polynomials P_i, $n = 0, 1, \ldots$ indicates the level of refinement, and $l = 0, 1, \ldots, 2^n - 1$ indexes the subinterval. These scaling functions are orthonormal for a fixed n and form a complete basis in the limit $n \to \infty$ for a given value of k. The condition for ending refinement is checked using the wavelet coefficients in the following way: For any n, let V_n be the space of all scaling functions at the nth level of refinement. This space is a subspace of V_{n+1}. Put another way,

$$V_0 \subset V_1 \subset V_2 \subset \cdots. \tag{13}$$

The space W_n is defined as the complement of V_n in V_{n+1}. Then, another way to write V_{n+1} is

$$V_{n+1} \equiv V_0 \oplus W_0 \oplus W_1 \oplus \cdots \oplus W_n. \tag{14}$$

This space W_n is spanned by a set of multiwavelets that can be constructed from the functions spanning V_{n+1} (Ref. 15). By this construction, the wavelet basis functions are mutually orthogonal across all refinement levels and orthogonal to all scaling functions at the same and coarser levels. The resulting vanishing moments of these functions mean that functions that are smooth (as many physically relevant integral operators are) have sparse representations in the multiwavelet basis.

By the relationship shown in Eq. (14), the projection of some function in W_n can be seen as the error in representing the said function in V_n as opposed to V_{n+1}. Thus, the wavelet basis coefficients provide a measure of when refinement can be stopped, and adaptivity is achieved by repeating this treatment individually for each subinterval. Through this method of refinement, any finite but arbitrary bound on the 2-norm of the error in the function representation can be enforced.[13,15]

Because the basis functions are discontinuous, derivative operators in the multiwavelet basis do not exist in the traditional sense. However, one can construct transition matrices for the derivative in the weak form, as is done in Ref. 15. Derivatives constructed in this manner will be used to apply the directional derivatives present in h_d of Eq. (8). Straightforward application of integral operators over more than one dimension is prohibitively expensive in the multiwavelet basis. Therefore, efficient application of integral operators in this basis requires constructing separated representations. Here, this is accomplished for the integral operator necessary in applying G_i by representing the bound-state Helmholtz Green's function as a sum of Gaussians via numerical integration of the following relation, as is done in Ref. 13:

$$\frac{e^{-\mu r}}{r} = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-r^2 e^{2s} - \mu^2 e^{-2s} + s} ds \tag{15}$$

for $\mu \geq 0$. In the case $\mu = 0$, Eq. (15) gives the Coulomb operator, which is required in application of the J and K operators. One key feature of MADNESS is the ability to represent a function either in the basis of scaling functions or in the "compressed" form of scaling functions and multiwavelets. Transformation between the two representations is fast and unitary, giving MADNESS the ability to quickly and accurately switch to the representation best suited to each operation.

II. METHODS

Equation (6) leads to a method of iterating a function represented in the multiwavelet basis to convergence. Letting n represent the calculation iteration, we have

$$\varphi_i^{n+1} = G_i^n(\mathbf{r}) * \left[(K - J - V)\varphi_i^n(\mathbf{r}) \right], \tag{16}$$

$$\varepsilon_i^n = \frac{\langle \varphi_i^n | h_d + J - K + V | \varphi_i^n \rangle}{\langle \varphi_i^n | \varphi_i^n \rangle}. \tag{17}$$

This iteration is motivated by the successful application of a similar one for nonrelativistic quantum Monte Carlo calculations by Kalos[16] and the subsequent extension to the multiwavelet basis by Harrison *et al.*[13] Here, we extend it to the relativistic case.

It is worth noting that there are three different possibilities for application of the Green's function [Eq. (8)]. Given some 4-component wavefunction $\phi(r)$, the convolution with G can be written as (omitting subscripts for brevity)

$$G * \phi = \frac{1}{2mc^2} (\phi * ([h_d + \varepsilon]g))$$

$$= \frac{1}{2mc^2} [h_d + \varepsilon](\phi * g)$$

$$= \frac{1}{2mc^2} (([h_d + \varepsilon]\phi) * g).$$

The three different formulations are analytically equivalent; however, there is a computational trade-off. The first formulation is numerically preferable due to the error-smoothing effect of the integral operators, as long as care is taken when constructing the derivative of g. However, the second method is considerably faster, due largely to the low cost of applying a derivative operator compared to an integral operator, and any loss of precision has been observed to be negligible for the systems studied here. Therefore, in all MADNESS calculations reported, the second method has been used. The third formulation has not been studied but is included for completeness.

Starting guesses are generated from a nonrelativistic Hartree-Fock routine, either generated by MADNESS's own or generated by NWChem[17] and then projected into the multiwavelet basis. For a spin-restricted orbital, one nonrelativistic spatial function (here, represented with the single-valued function φ_{nr}) generates two starting guesses, each representing one electron, in the following way: Two values for the large component are chosen as

$$\varphi_l = \begin{bmatrix} \varphi_{nr} \\ 0 \end{bmatrix} \quad \text{or} \quad \varphi_l = \begin{bmatrix} 0 \\ \varphi_{nr} \end{bmatrix}, \tag{18}$$

and in each case, the small component is initialized as

$$\varphi_s = \frac{1}{2c} \boldsymbol{\sigma} \cdot \mathbf{p} \varphi_l \tag{19}$$

in order to maintain the correct nonrelativistic relationship between the large and small components. For a spin-unrestricted orbital, each nonrelativistic spatial function instead only generates one starting guess. It should be noted that in practice, to prevent loss of accuracy by frequent multiplication of c, the small component is stored and computed with $c\varphi_s$ and is rescaled by c^{-1} as needed for computation of properties.

Following construction of the initial guess function, the overall algorithm for the ground-state energy calculation emulates that in Ref. 13 and involves the following:

1. Computation of the Fock matrix in the space of occupied orbitals.
2. Diagonalization of the Fock matrix in the space of occupied orbitals and transformation of the occupied orbitals, as well as exchange orbitals, into the eigenbasis.
3. Convolution with the Green's function [Eq. (8)].
4. Application of the Krylov-Accelerated Inexact Newton (KAIN) solver.[18]
5. Orthogonalization of the orbitals.
6. Application of exchange, Coulomb, and nuclear potential operators for the next iteration. Calculation of updated orbital energy.

Some notes on implementation: The ordering of the above algorithm implies that the result of applying the potential to each initial guess orbital has been computed before iterating. In addition, because the KAIN solver requires a consistent history of orbitals, arbitrary phases as well as rotations within degenerate eigenspaces, introduced by the eigensolver used in the diagonalization step, must be removed.

All calculations were performed without spatial or time-reversal symmetry, meaning the code computes with one (four-component) wavefunction in 3D-space for each electron.

III. RESULTS

In MADNESS, the user may select the number of scaling functions (derived from Legendre polynomials) to use in each refined interval (defined with k) as well as the tolerance (enforced on the 2-norm of the error in the function) for refinement. All MADNESS calculations reported in this paper used $k = 8$ and a tolerance of 10^{-6}. An internal parameter determines whether the refinement tolerance is enforced on a function itself or on both the function and its first derivative. While the latter setting does increase the accuracy of calculation, it also substantially increases the memory requirement of the computation. Therefore, for these calculations, this parameter was left at the former setting.

Tables I and II show the results of Dirac-Fock calculations on atoms and molecules, respectively. In the case of atoms, comparisons are to GRASP[4] code calculations from the literature (Ref. 9), and both codes use a Fermi nuclear charge distribution model.[9] Note that the potential due to a Fermi nuclear charge model has no analytic form. Instead, the nuclear charge distribution is projected into the multiwavelet basis, and application of the Coulomb operator [Eq. (15) for $\mu = 0$] yields the potential.

In the case of molecules, comparison is to the DIRAC relativistic quantum chemistry package[19] using the built-in all-electron double-, triple-, and quadruple-zeta basis sets of Dyall[20–22] with $\langle SS|SS \rangle$ integrals computed explicitly, and both codes instead use a Gaussian nuclear charge distribution model.[9] All numbers (both atomic and molecular) reported are rounded at the 5th decimal place. The MADNESS Dirac-Fock code was able to reproduce the total energies calculated by GRASP to at least six significant digits. For molecules, MADNESS was able to obtain energies similar

TABLE I. Comparison of MADNESS and GRASP Dirac-Fock ground state energy calculations for atoms.

Atom	MADNESS	GRASP	Error	Relative error
Be	-14.57589	-14.57589	-9.7×10^{-7}	6.7×10^{-8}
Ne	-128.69194	-128.69193	-8.9×10^{-6}	6.9×10^{-8}
Mg	-199.93509	-199.93507	-2.1×10^{-5}	1.1×10^{-7}
Ar	-528.68380	-528.68376	-3.6×10^{-5}	6.8×10^{-8}
Ca	-679.71020	-679.71016	-3.9×10^{-5}	5.7×10^{-8}
Zn	-1794.61301	-1794.61297	-3.1×10^{-5}	1.7×10^{-8}
Kr	-2788.86065	-2788.86058	6.8×10^{-5}	2.4×10^{-8}
Sr	-3178.07990	-3178.07991	8.1×10^{-6}	-2.5×10^{-9}
Cd	-5593.31896	-5593.31845	-5.1×10^{-4}	9.2×10^{-8}
Xe	-7446.89475	-7446.89439	-3.6×10^{-4}	4.9×10^{-8}
Ba	-8135.64361	-8135.64358	-2.9×10^{-5}	-3.6×10^{-9}
Yb	-14067.66461	-14067.66691	2.3×10^{-3}	-1.6×10^{-7}
Hg	-19648.85095	-19648.85822	7.3×10^{-3}	-3.7×10^{-7}
Rn	-23602.01258	-23602.02331	1.1×10^{-2}	-4.5×10^{-7}

TABLE II. Comparison of MADNESS and DIRAC Dirac-Fock ground state energy calculations for molecules.

Molecule	ae2z	ae3z	ae4z	MADNESS
HF	-100.15191	-100.16204	-100.16304	-100.16318
N_2	-109.04190	-109.05743	-109.05920	-109.05940
BH_3	-26.40518	-26.40948	-26.40993	-26.41000
H_2O	-76.11124	-76.12201	-76.12327	-76.12345
H_2S	-399.81930	-399.83796	-399.83893	-399.83902
H_2Se	-2429.75303	-2429.79462	-2429.79571	-2429.79572
H_2Te	-6794.85830	-6794.87655	-6794.87733	-6794.87704
H_2Po	-22232.15669	-22232.17686	-22232.17807	-22232.17591

to the corresponding DIRAC basis-set calculations; however, direct comparison between the fully numerical MADNESS results and the basis-set DIRAC results is not straightforward due to the possibility of prolapse.[23,24]

To give the reader an idea of the scale of a MADNESS Dirac-Fock calculation, we describe the calculation of the ground state of Rn. In this case, each orbital is represented with a total of $O(10^6)$ coefficients across all four components. The maximum depth of the refinement tree over all orbitals is 18 levels. With an interval of computation of $[-50, 50]^3$ atomic units, the smallest box for which coefficients are computed has a side length of $2^{-18} \approx 3.8 \times 10^{-4}$, which is approximately the scale at which the nuclear charge distribution becomes smooth. All MADNESS calculations were run using 16 nodes with 40 Intel Skylake cores per node (2.1 GHz). The average time per iteration for the Rn calculation was about 627 s.

A detailed cost comparison between codes is omitted, as this study merely seeks to demonstrate accuracy, and the MADNESS Dirac-Fock code is currently lacking many potential optimizations. However, a few statements can be made about the multiwavelet code: The number of iterations required for convergence increases with the charge of the nucleus. We suspect that this is due to the

nonrelativistic solution being a poor initial guess for those systems with highly charged nuclei. Analytically, the cost per iteration scales quadratically with respect to the number of electrons; however, the systems reported in this paper are not large enough to see the asymptotic scaling.

The MADNESS Dirac-Fock code maintains relative errors consistent with the truncation threshold, as shown in Table I. The desired accuracy is a parameter selected by the user, and the computational cost increases accordingly.

IV. CONCLUSIONS

For the first time, a fully numerical approach to four-component relativistic quantum chemistry calculations for general molecules has been described and demonstrated. In this approach, the single-particle Dirac Green's function is used to form an integral equation that can be iterated to solution. The said iteration is accomplished in the multiresolution multiwavelet basis via the software package MADNESS. The accuracy of this method is demonstrated through Dirac-Hartree-Fock calculations of the ground state energies of several atoms and molecules, with comparisons made

to GRASP and DIRAC. While this approach is unlikely to replace grid-based calculations for atoms in the near future, to the best of our knowledge it is the only fully numerical approach for general molecules.

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