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ARTICLE

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

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 [illegible]

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

$$\varphi_i^{n+1} = G_i^n(\mathbf{r}) \square [(K - J -$$

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

Atom	MADNESS	GRASP	Error	Relative error
Be	−14.575 89	−14.575 89	-9.7×10^{-7}	6.7×10^{-8}
Ne	−128.691 94	−128.691 93	-8.9×10^{-6}	6.9×10^{-8}
Mg	−199.935 09	−199.935 07	-2.1×10^{-5}	1.1×10^{-7}
Ar	−528.683 80	−528.683 76	-3.6×10^{-5}	6.8×10^{-8}
Ca	−679.710 20	−679.710 16	-3.9×10^{-5}	5.7×10^{-8}
Zn	−1 794.613 01	−1 794.612 97	-3.1×10^{-5}	1.7×10^{-8}
Kr	−2 788.860 65	−2 788.860 58	6.8×10^{-5}	2.4×10^{-8}
Sr	−3 178.079 90	−3 178.079 91	8.1×10^{-6}	-2.5×10^{-9}
Cd	−=			

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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