

# All-electron four-component Dirac-Kohn-Sham procedure for large molecules and clusters containing heavy elements

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In exploiting state-of-the-art density fitting algorithms, we show that relativistic four-component Dirac-Kohn-Sham computations using  $G$ -spinor basis sets and Hermite Gaussian fitting functions can readily be applied to large molecular systems, including large clusters of heavy atoms. The inherent accuracy of the fitting procedure is discussed and the techniques to ensure high accuracy are mentioned. The power of the method, with its reduced scaling with respect to size and a prefactor shrunk by several orders of magnitude, is illustrated through some all-electron test calculations on gold clusters up to Au<sub>16</sub>.

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The predictive modeling of molecules, clusters, and nano-scale materials containing heavy atoms represents a particularly challenging task for theory and computational science because both relativity and electronic correlation play crucial roles in determining their electronic structure and properties. The most rigorous way to introduce relativity in the modeling of molecular systems is to use the four-component formalism derived from the Dirac equation.<sup>1</sup> The full four-component formalism is particularly appealing because it affords a physical clarity that is absent in the two-component reductions of the Dirac operator, especially with regard to the problems involved in the change of representation and the gauge dependencies of the electromagnetic interaction. It also represents the most rigorous way of treating explicitly and *ab initio* all interactions involving spin, which are today of great technological importance and are receiving growing theoretical attention.<sup>2</sup> The successful attack on numerous other important scientific challenges depends heavily on the availability of fast four-component all-electron methodologies concerning, for example the nuclear properties of both light and heavy atoms, parity violation in molecules, electric and magnetic properties of molecules in strong fields, and the basic nature of chemical bonds involving both heavy and superheavy elements (see, e.g., Refs. 3). However, only relatively recently have significant developments taken place making the four-component framework suitable for practical applications.<sup>4-6</sup>

Four-component calculations have an intrinsically greater computational cost than analogous nonrelativistic or less rigorous quasirelativistic approaches but this essentially involves only a larger prefactor in the scaling with respect to a number of particles or basis set sizes, not a more unfavorable power law. Therefore, while computationally less demanding schemes have been devised involving reduced Hamiltonians (see, e.g., Ref. 7 and references therein) or, in a recent proposal, a four-component scheme where the negative-energy states are kept frozen at atomic contributions,<sup>8</sup> the applicability of the four-component theory to large molecular systems is hindered mainly by the comparatively early stage of development of the relevant algorithms and codes, and not by any fundamental problem of principle.

Another crucial aspect of the theoretical chemistry of

heavy atoms is that of electron correlation. For polyatomic systems containing heavy elements, explicit electron correlation methods rapidly exceed feasibility limits because of the adverse scaling behavior and large number of electrons involved, while linear scaling techniques<sup>9</sup> lose their computational advantages due to the compactness of the molecular systems. A far more practicable approach is the density functional theory (DFT),<sup>10</sup> where all the exchange-correlation effects are expressed implicitly as a functional of the electron density or, more generally, the charge-current density; intensive research is under way in this area.<sup>11</sup> The relativistic four-component generalization of the Kohn-Sham method is referred to as the Dirac-Kohn-Sham (DKS) model.<sup>12</sup> Several modern implementations of this theory are available,<sup>5,6,13</sup> including in our own program BERTHA.<sup>14-17</sup>

In this Brief Report, we present a significant step forward in the effective implementation of the four-component DKS theory, based on the electron-density fitting approach that is already widely used in the nonrelativistic context. In addition to a reduction in the scaling law with respect to the number of heavy atoms and the size of the basis set, we demonstrate a dramatic reduction, by several orders of magnitude, in the scaling prefactor that enables the fully relativistic study of large polyatomic systems. The inherent accuracy of the fitting procedure and the numerical techniques that are necessary to ensure high accuracy are also discussed.

In the simplest DKS formulation, the exchange-correlation potential of nonrelativistic Kohn-Sham theory may be augmented by relativistic corrections. In order to represent the four-component solutions of the DKS equation in BERTHA, we adopt a Gaussian basis set expansion. In particular, the large ( $L$ ) and small ( $S$ ) components of the spinor solutions are expanded as a linear combination of  $G$ -spinor basis functions. Each  $G$ -spinor component ( $L$  or  $S$ ) is a two-component spinor function of spherical Gaussian type. This choice of basis set has several theoretical advantages<sup>14,15</sup> and, above all, it preserves all the computational advantages that have made Gaussian-type functions the most widely used expansion set in computational quantum chemistry. A peculiar and important feature of our approach is that the density elements  $\rho_{\mu\nu}^{TT}(\mathbf{r})$ , which are the scalar products of pairs of  $G$ -spinors labeled as  $\mu$  and  $\nu$  ( $T=L, S$ ), are evaluated

as finite linear combinations of scalar auxiliary Hermite Gaussian-type functions (HGTFs) by analogy to the McMurchie–Davidson expansion of the nonrelativistic charge density.<sup>18</sup> It is this formulation<sup>14</sup> that enables the highly efficient analytic computation of all the required multicenter  $G$ -spinor interaction integrals.

Normally, the construction of the Coulomb and exchange-correlation matrices dominate the computational cost of a conventional DFT calculation. A widely used device to accelerate nonrelativistic DFT computations replaces the exact electron density, obtained directly from the orbital amplitudes, by an approximate fitted density constructed using a suitable auxiliary basis set,  $\{f_i(\mathbf{r})\}$ . The most successful scheme to obtain an accurate and stable approximate density in nonrelativistic quantum chemistry is the Coulomb fitting method.<sup>19</sup> In this scheme, the expansion coefficients of the auxiliary functions are determined by minimizing the mean-square error in the Coulomb energy. A great advantage of this approach is that the fitting error in the Coulomb energy is intrinsically non-negative so that it may be minimized variationally. We have recently introduced an efficient Coulomb fitting scheme in our DKS method<sup>16</sup> using an auxiliary set of HGTF fitting functions. We have shown that a single set of functions may be used to fit both the large- and small-component contributions to the density. The method results in a symmetric, positive-definite linear system to be solved in order to obtain the vector of fitting coefficients. The procedure involves only the calculation of two-center Coulomb integrals over the fitting set,  $A_{ij} = \langle f_i | f_j \rangle$ , and three-center integrals between the fitting functions and density overlaps,  $I_{i,\mu\nu}^{TT} = \langle f_i | \rho_{\mu\nu}^{TT} \rangle$ . The formal scaling is reduced from  $O(N^4)$  to  $O(N^3)$  in the evaluation of the Coulomb contribution in this approach. In our implementation, we take further advantage of a relativistic generalization of the  $J$ -matrix algorithm and an additional simplification arising from the use of primitive HGTFs that are grouped together in “shell” sets with increasing angular momentum but sharing a common exponent.<sup>16</sup> This permits the use of the efficient recurrence relations for Hermite polynomials in the computation of the two-electron repulsion integrals.

With the above strategy, the bottleneck of a four-component DKS calculation has been moved entirely to the computation of the exchange-correlation matrix contribution. It is precisely this problem that we address in this Brief Report, extending the density fitting technique to the calculation of the relativistic exchange-correlation term. The idea of using the density resulting from the Coulomb fitting to compute directly the exchange-correlation functional has been proposed previously in the nonrelativistic framework<sup>20</sup> and some effective implementations have been reported recently.<sup>21</sup> The approximate DKS exchange-correlation matrix elements are

$$\tilde{K}_{\mu\nu}^{TT} = \frac{\partial E_{xc}[\tilde{\rho}]}{\partial D_{\mu\nu}^{TT}} = \int \frac{\delta E_{xc}[\tilde{\rho}]}{\delta \tilde{\rho}(\mathbf{r})} \frac{\partial \tilde{\rho}(\mathbf{r})}{\partial D_{\mu\nu}^{TT}} d\mathbf{r}, \quad (1)$$

where  $\tilde{\rho}$  is the fitted density,  $D_{\mu\nu}^{TT}$  are the elements of the density matrix, and the functional derivative of the exchange-correlation energy  $E_{xc}$  with respect to the density

defines the exchange-correlation potential  $v_{xc}[\tilde{\rho}(\mathbf{r})]$ . Using the electronic density obtained by the variational Coulomb fitting scheme, one then has<sup>16,21</sup>

$$\frac{\partial \tilde{\rho}(\mathbf{r})}{\partial D_{\mu\nu}^{TT}} = \sum_i \frac{\partial c_i}{\partial D_{\mu\nu}^{TT}} f_i(\mathbf{r}) = \sum_{i,j} A_{ij}^{-1} I_{j,\mu\nu}^{TT} f_i(\mathbf{r}), \quad (2)$$

where  $\{c_i\}$  are the fitting coefficients. Substituting Eq. (2) into Eq. (1), we obtain a very simple expression for the exchange-correlation matrix elements,

$$\tilde{K}_{\mu\nu}^{TT} = \sum_{i,j} A_{ij}^{-1} w_i I_{j,\mu\nu}^{TT} = \sum_j z_j J_{j,\mu\nu}^{TT}, \quad (3)$$

where  $z_j$  are the elements of a vector  $\mathbf{z}$ , which is the solution of the linear system,

$$\mathbf{A}\mathbf{z} = \mathbf{w}. \quad (4)$$

The vector  $\mathbf{w}$  is the projection of the “fitted” exchange-correlation potential onto the auxiliary functions,

$$w_i = \int v_{xc}[\tilde{\rho}(\mathbf{r})] f_i(\mathbf{r}) d\mathbf{r}. \quad (5)$$

Once the vectors  $\mathbf{c}$  and  $\mathbf{z}$  have been computed, the Coulomb and exchange-correlation contributions to the DKS matrix can be formed in a single step,

$$\tilde{J}_{\mu\nu}^{TT} + \tilde{K}_{\mu\nu}^{TT} = \sum_i I_{i,\mu\nu}^{TT} (c_i + z_i). \quad (6)$$

The elements of the vector  $\mathbf{w}$ , involving integrals over the exchange-correlation potential, are computed numerically by a cubature scheme already in place.<sup>15</sup> However, it is important to note that the cost of this step tends to become negligible compared to that of the conventional numerical integration step as the size of the system increases: the latter scales as  $N^2 \cdot N_g$ , where  $N$  is the number of  $G$ -spinor basis functions and  $N_g$  is the number of grid points. Using the fitted density, the scaling reduces to  $N_f \cdot N_g$ , where  $N_f$  is the number of auxiliary basis functions used to fit the density. Furthermore, in the integration procedure, we can take advantage of our particular choice of auxiliary functions; the use of primitive HGTFs that are grouped together in sets sharing the same exponent minimizes the number of expensive exponential evaluations at each grid point. Further computational savings arise from using the recurrence relations for Hermite polynomials in the evaluation of the angular part of the auxiliary fitting functions and their related derivatives. All of these advantages are especially welcome because we have found that it is particularly important to ensure high accuracy in the numerical integration if the propagation of errors that arise in the solution of the linear system [Eq. (4)] into the explicit matrix representation of the exchange-correlation [Eq. (3)] is to be avoided. The significant gains made in the efficiency of numerical integration may be exploited without impairing the computational advantages of the approach by adopting integration grids that are sufficiently dense to ensure accuracy.

Before showing in detail the practical computational power of the DKS approach outlined above, a brief discussion of the accuracy of the general fitting procedure is in

order. The variational approach employed in the fitting of the density and in the optimization of the auxiliary basis sets for atoms and small molecules usually yields a very accurate and systematically improvable value of the Coulomb energy. It is, however, not necessarily the case that the Coulomb-fitted density produces a similarly accurate value of the exchange-correlation energy or, by extension, the total energy. We find that significant errors, of the order of several millihartree at best, typically occur. The resolution of this problem, which has been largely ignored in the extant literature, will be discussed in detail in a dedicated study<sup>22</sup> and we only briefly summarize it here. In order to obtain an accurate total energy, one should explicitly optimize the auxiliary basis set for both the Coulomb and exchange-correlation energy functionals at the same time, but this is generally troublesome and time consuming. Simple recipes for extending the auxiliary basis set starting from the Coulomb-optimized set have also been proposed,<sup>21</sup> but we have found that such procedures do not always work in the relativistic context; it may even be the case that augmenting the auxiliary basis makes the total energy less accurate. In the spirit of Ref. 23, we have found a simple and particularly effective procedure, in which the auxiliary fitting basis set is constructed dynamically from the underlying  $G$ -spinor basis, reproducing accurately the total energy of the unfitted density. In this approach, however, the final auxiliary basis is generally larger than that of a standard Coulomb fitting procedure, which inevitably increases the computational cost. One should also always bear in mind that general basis optimization may introduce a strong dependence on the particular exchange-correlation functional that is used. A more general approach that yields accurate total energies without any optimization procedure has also been investigated by us. This is based on the observation that the electron density obtained by making the approximate total-energy functional stationary with respect to variations in the orbital spinor coefficients gives, in turn, a total energy that is almost exactly coincident with that obtained without density fitting. The total energy calculated using the converged density in a simple “restart” procedure compensates almost exactly for the use of a fitted density in the Coulomb and exchange-correlation interactions. This is a very general result that holds even when an auxiliary fitting basis set of moderate size is used, which will be discussed in detail in a future paper.<sup>22</sup>

As an illustrative example that further clarifies the issues discussed above, we summarize the results of calculations on

$\text{Au}_2$  performed with the BLYP exchange-correlation functional<sup>24</sup> and a  $G$ -spinor basis set of size  $22s19p12d8f$  (Ref. 25) for the large component; the corresponding small-component basis was generated using the restricted kinetic balance relation.<sup>14</sup> Two auxiliary sets of fitting functions have been used: a standard Coulomb-optimized basis set, denoted B20, consisting of 307 HGTFs per atom,<sup>16</sup> and a basis set obtained by the “dynamic” procedure mentioned above, labeled B22-xc (444 HGTFs per atom). Calculations were carried out at a range of Au-Au distances from 2.1 to 3 Å. The standard B20 auxiliary basis fits the density of  $\text{Au}_2$  at its equilibrium distance with an error in the Coulomb energy of just 7  $\mu$ hartree, but the error in the total energy is three orders of magnitude larger at  $\approx 5$  mhartree. In both cases, the error is essentially constant over the entire range of Au-Au separations. With the B22-xc basis generated by our procedure, the error in the total energy drops to about 20  $\mu$ hartree and is again nearly independent of internuclear separation. Finally, using the “restart” procedure of performing an additional total-energy calculation with the final true density reduces the B20 error to only 16  $\mu$ hartree. The same procedure with the B22-xc set makes the error vanish to working accuracy. As just mentioned, all computed energy curves are accurately parallel over the internuclear range investigated and this is reflected in the nearly invariant calculated spectroscopic properties, which also coincide precisely with the values resulting from calculations without density fitting. We have also tested the accuracy of our fitting schemes in a system containing both heavy and light atoms by computing the reduction energy of a water molecule from the cluster  $\text{Au}(\text{H}_2\text{O})_9^+$ . Here, the error due to the density fitting is only about 3 meV while, again, practically exact results are obtained if we calculate total energies using the true density obtained at self-consistent field (SCF) convergence. Complete details of the calculations will be reported in Ref. 22.

We finally turn to an illustration of the efficiency and scaling of our DKS density fitting, which is the main motivation of the present Brief Report. We performed DKS calculations for several gold clusters of varying size up to  $\text{Au}_{16}$ , both with the conventional DKS scheme and using the density fitting approach described here. Time-reversal symmetry was not used in the calculations so that each of the Kramer pair orbital spinors have been handled independently. This means that clusters of doubled size could be treated at similar cost. A very fine integration grid has been employed for

TABLE I. DKS matrix size, CPU times (s) for the construction of the Coulomb ( $\mathbf{J}$ ) plus exchange-correlation ( $\mathbf{K}$ ) matrices in the conventional (“conv”) and density fitting (“fit”) schemes, resulting speed ratio, and DKS matrix diagonalization times (s) (“Diag”) for various gold clusters.

Cluster	DKS size	$(\mathbf{J}+\mathbf{K})_{\text{conv}}$	$(\mathbf{J}+\mathbf{K})_{\text{fit}}$	Speed-up	Diag <sup>a</sup>
$\text{Au}_2$	1560	$1.86 \times 10^3$	7.4	251	24.7
$\text{Au}_4$	3120	$1.71 \times 10^4$	44.1	388	184
$\text{Au}_8$	6240	$1.71 \times 10^5$	296	578	$1.50 \times 10^3$
$\text{Au}_{16}$	12480	$1.91 \times 10^6$ <sup>b</sup>	$2.16 \times 10^3$	884	$1.21 \times 10^4$

<sup>a</sup>Using the standard LAPACK routine zhegv (Ref. 26).

<sup>b</sup>Extrapolated value.

maximum accuracy, with 122 400 grid points for each gold atom. The B20 auxiliary basis set has been used for density fitting. All calculations were carried out on one processor of a biprocessor node Intel(®) Xeon(®) CPU 3.00GHz node. The timings measured for the evaluation of the Coulomb and exchange-correlation matrix contributions are collected in Table I. The reduction of the computational cost by the use of the density fitting scheme is evident. The data show that the time for the construction of the  $\mathbf{J}+\mathbf{K}$  matrix scales as  $N^{3.5}$  for the conventional scheme and only as  $N^{2.9}$  using density fitting, where  $N$  is the number of atoms. It is very important to note, furthermore, that the scaling prefactor drops from 125 s in the standard procedure to 0.8 s in the density fitting scheme. This dramatic improvement can be enhanced further by exploiting a number of additional features. With the present implementation, the cost of the DKS matrix construction becomes a fraction of the diagonalization step. Therefore, because of the one-to-one mapping between the large and small components of the  $G$ -spinor basis set, the contraction of the primary basis would be particularly advantageous, since the dimension of the matrix representation could be dramatically reduced. Using the Poisson relation between the electrostatic Coulomb potential and the electronic density further simplifies the three-index two-electron repulsion integrals into overlap integrals.<sup>17,27</sup> This approach can be readily accommodated within the present scheme and very effectively reduces its scaling behavior. Finally, the scheme presented here lends itself to effective computational parallelization, along lines that have already been reported for the standard procedure.<sup>28</sup>

In this Brief Report we have demonstrated, using a work-

ing implementation, that the computational burden associated with the four-component structure of the Dirac operator can be greatly reduced by adopting computational strategies based on density fitting. In particular, we have extended the implementation of the density fitting approach both to the Coulomb and exchange-correlation matrix construction of the DKS method. While preserving high accuracy in the total energy through computational simple devices, the method exhibits highly advantageous scaling properties that may be further improved by the exploitation of density localization, as well as an extremely small scaling prefactor. In our current preliminary implementation, heavy atom clusters of the size of  $\text{Au}_{32}$  and beyond are already tractable with ease, preserving the full accuracy and physical transparency of the all-electron relativistic four-component formalism. This offers exciting opportunities in both the applicability and the development of relativistic quantum chemistry, bringing, in particular, realistic cluster science, catalysis, and superheavy element physics and chemistry within the reach of accurate theoretical modeling. On the development front, the efficiency of the density fitting techniques outlined in this paper could be exploited, for example, in (i) four-component post-SCF methods, requiring the evaluation of two-electron integrals over spinors, (ii) the implementation of real-time propagation theories and molecular property calculations, which may benefit from the significant gains reported here in four-component Hamiltonian matrix construction. It is worth noting that a rigorous current-density-functional theory (in either a spin-diagonalized or covariant representation) may be readily accommodated in our present scheme using essentially the same fitting techniques described here.

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