Poisson-transformed density fitting in relativistic four-component Dirac–Kohn–Sham theory

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We present recent developments in the implementation of the density fitting approach for the Coulomb interaction within the four-component formulation of relativistic density functional theory [Belpassi et al., J. Chem. Phys. 124, 124104 (2006)]. In particular, we make use of the Poisson equation to generate suitable auxiliary basis sets and simplify the electron repulsion integrals [Manby and Knowles, Phys. Rev. Lett. 87, 163001 (2001)]. We propose a particularly simple and efficient method for the generation of accurate Poisson auxiliary basis sets, based on already available standard Coulomb fitting sets. Just as is found in the nonrelativistic case, we show that the number of standard auxiliary fitting functions that need to be added to the Poisson-generated functions in order to achieve a fitting accuracy equal or, in some cases, better than that of the standard procedure is remarkably small. The efficiency of the present implementation is demonstrated in a detailed study of the spectroscopic properties and energetics of several gold containing systems, including the Au dimer and the CsAu molecule. The extraction reaction of a H2O molecule from a Au(H2O)6+ cluster is also calculated as an example of mixed heavy-light-atom molecular systems. The scaling behavior of the algorithm implemented is illustrated for some closed shell gold clusters up to Au12+. The increased sparsity of the Coulomb matrices involved in the Poisson fitting is identified, as are potential computational applications and the use of the Poisson fitting for the relativistic exchange-correlation problem. © 2008 American Institute of Physics. [DOI: 10.1063/1.2868770]

I. INTRODUCTION

Molecular systems, clusters, and materials containing heavy atoms have drawn considerable recent attention because of their rich chemistry. In order to model computationally systems containing heavy elements, the methods of relativistic quantum mechanics must be adopted because it is necessary to capture scalar and spin-dependent interactions that are neglected in the conventional nonrelativistic formulation of quantum chemistry. To complicate matters further, electron correlation also plays a crucial role in determining the electronic structure of these systems, and relativistic and correlation effects are, in general, not additive.1 Due to the large number of electrons that have to be correlated, explicit electron correlation methods rapidly exceed feasibility limits because of their adverse scaling behavior. A far more practicable approach is, in these cases, density functional theory (DFT), which is normally cast in the form of the independent-particle Kohn–Sham model, where all the exchange-correlation effects are expressed implicitly by a functional of the electron density (or current density). Thus, the problem of describing electron correlation is, in principle, reduced to the search of suitable exchange-correlation functionals. In this respect, new generations of functionals such as the optimized effective potentials and others hold much promise for transition and heavy elements. Nonetheless, the modeling of systems containing heavy elements still remains a particularly challenging arena for theoretical chemistry.

The extension of DFT to a relativistic four-component generalization of the Kohn–Sham method, referred to as the Dirac–Kohn–Sham (DKS) model, was formulated by Rajagopal and Callaway,2 Das et al.,3 and Macdonald and Vosko.4 Relativistic DFT has been implemented by several groups5–11 at different levels of approximation. In this context, the full four-component formalism has a great advantage 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. The full four-component DKS calculations have an intrinsically greater computational cost than analogous nonrelativistic approaches, mainly because of the four-component structure in the representation of the DKS equations, the complex matrix representation that usually arises as a consequence, and the increased work involved in the evaluation of the electron density from the spinor amplitudes. However, despite this increased computational burden, the relativistic four-component formulation does not introduce any new unfavorable scaling with respect to the number of particles or the number of basis functions.

As in nonrelativistic DFT a computationally demanding step in DKS is the problem of describing all of the electro-
static Coulomb interactions in the system. Here, an important tool in most of modern DFT codes consists in taking advantage of density fitting procedures,\cite{12} which employ auxiliary basis functions to represent the electron density. Through this device, the four-center two-electron repulsion integrals are decomposed into three- and two-center integrals, reducing both the formal scaling of the Kohn–Sham problem from O(N⁴) to O(N³) and the associated scaling prefactor. Over the years, much sophistication has been brought to this basic idea. Recently a linear scaling implementation of the density fitting method has been proposed by Sodt et al.\cite{13} Other recent methodological developments are well summarized in the Introduction of Ref. 13. Numerical density fitting approaches based on an atomic multipolar expansion\cite{14} and on a least-squares fit\cite{15} have also been employed in the four-component relativistic domain.

Manby et al.\cite{16,17} investigated the use of the Poisson equation within the standard density fitting scheme, showing that most of the two-index and three-index electron repulsion integrals may be reduced to simpler overlaplike integrals without significant impact on the accuracy of the fitting procedure. This result translates into a great saving in the number of integrals to be computed. This “Poisson trick” has been adopted not only in DFT but also in other methods such as fast Hartree–Fock and local density fitting post-Hartree–Fock methods. Once adapted to periodic boundary condition, it has also turned out to be a key step for the efficient implementation of the density fitting procedure for the study of periodic systems.\cite{18,19} A promising linear scaling method, also based on the Poisson equation, for the evaluation of the Coulomb integrals has been proposed very recently by Kurashige et al.\cite{20} The purpose of the present paper is to extend the Poisson scheme to the Coulomb problem in four-component relativistic DFT. This represents an important development of our recent introduction of the standard density fitting method into the framework of relativistic four-component DFT using G-spinor relativistic basis sets.\cite{21} As with previous developments, we have implemented the present formalism in the DKS module of the relativistic code BERTHA.\cite{9,22,23,24,25}

In the next section, we first briefly review, as a convenient reference background, the standard density fitting approach in the context of DKS theory. In Sec. III we then present a detailed description of the relativistic extension of the density fitting scheme based on the Poisson equation. Finally, the generation of suitable auxiliary basis sets, the accuracy of our implementation, and its computational efficiency are discussed in the Sec. IV.

II. THEORETICAL BACKGROUND

A. The Dirac–Kohn–Sham equation and the relativistic density fitting approach

The DKS equation, considering only the longitudinal electrostatic interactions, reads
\begin{equation}
\{c \alpha \cdot p + \beta c^2 + v^L(r)\} \Psi_j(r) = E_j \Psi_j(r),
\end{equation}
where the diagonal potential operator \(v^L(r)\) is given by the sum of three terms,
\begin{equation}
v^L(r) = v_{\text{ext}}(r) + v_{\text{H}}^L(\rho(r)) + v_{\text{xc}}^L(\rho(r)).
\end{equation}
The external potential due to the fixed nuclei is denoted \(v_{\text{ext}}(r)\), and \(v_{\text{H}}^L(\rho(r))\) represents the electronic Coulomb interaction, which is a functional of the relativistic charge density \(\rho(r)\). The term denoted \(v_{\text{xc}}^L(\rho(r))\) is the relativistic longitudinal exchange-correlation potential, whose exact form is, like that of the corresponding nonrelativistic quantity, unknown and has to be approximated. The common nonrelativistic density functional may be used as a first reasonable approximation to which relativistic corrections may be added.\cite{10,26}

To represent the four-component solutions of Eq. (1), the formalism we adopt, and which is the foundation of the BERTHA program, uses a Gaussian basis set expansion of G-spinor functions.\cite{9} G-spinors are themselves two-component functions of spherical Gaussian type,\cite{27} which serve as a basis for four-component molecular spinors. This basis does not suffer from the variational problems of kinetic balance\cite{28} if a finite nuclear charge distribution is employed but balance\cite{28} if a finite nuclear charge distribution is employed.

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\[ H_0[\alpha;i,j,k] = \sum_{T=L,S} \sum_{\mu,\nu} E_{ij}^{TT}[\mu,\nu;i,j,k] D_{\mu\nu}, \]  

(5)

where the second sum on the right runs over all basis function pairs resulting, by the Gaussian product theorem, in the origin and exponent labeled by \( \alpha \). \( D^{LL} \) and \( D^{SS} \) are the large- and small-component density matrices, respectively.

In the DKS theory, the matrix representations are necessarily larger than their nonrelativistic counterparts, and they are intrinsically complex for some symmetry types. The construction of the DKS matrices and, in particular, the evaluation of the Coulomb (\( J \)) and exchange-correlation (\( K \)) contributions dominate the computational cost of the calculation. As in the case of the density, these matrices are composed of two diagonal blocks, corresponding to the large-large and small-small component interactions. The evaluation of the exchange-correlation term is carried out by numerical integration procedures.\(^9\) In particular, multiconfiguration integrals over functionals involving \( \varrho(r) \) and \( |\nabla \varrho(r)| \) are evaluated efficiently using methods based on those described by Becke.\(^{33} \)

Using density fitting techniques for the computation of these matrix elements has been shown to be highly effective in nonrelativistic DFT. We are currently developing and implementing the four-component relativistic variant of this approach, which will be described in a forthcoming paper.\(^{34} \)

This density matrix representation is inherently sparse because of the local nature of the exchange-correlation potential, a feature that may be exploited in the construction of linear scaling algorithms. The Coulomb interaction matrix is constructed analytically in BERTHA, using an efficient relativistic generalization of the \( J \)-matrix method of Almlöf.\(^{31,32} \)

We have recently implemented an effective density fitting procedure for the four-component DKS Coulomb problem exploiting this technique.\(^{21} \) As a convenient starting point for the discussion in the next section, we briefly repeat here the main features of this approach as it is implemented in BERTHA.

Exactly as in the nonrelativistic theory, the total relativistic density is expanded in a set of \( N_s \) real auxiliary basis functions \( \{f_s(r)\} \) according to

\[ \varrho(r) = \sum_{s=1}^{N_s} d_s f_s(r). \]

(6)

The tilde over the fitted density \( \tilde{\varrho}(r) \) is used to distinguish it from the exact one \( \varrho(r) \). The auxiliary basis functions make up a unique set for both the large and small components of the density. The coefficients \( d_s \) are chosen to minimize an error metric of the form

\[ \Delta = \int dr \int dr' \left[ \varrho(r) - \tilde{\varrho}(r) \right] \left[ \varrho(r') - \tilde{\varrho}(r') \right], \]

(7)

which also minimizes the error in the Coulomb energy.

The above condition leads to a linear system for the vector of fitting coefficients \( \mathbf{d} \), where

\[ \mathbf{Ad} = \mathbf{v}. \]

(8)

The real, symmetric, and positive-definite matrix \( \mathbf{A} \) is the representation of the Coulomb interaction in the auxiliary basis,

\[ A_{\mu \nu} = \langle f_s \| f_{s'} \rangle = \int f_s(r) \left[ \frac{1}{|r - r'|} \right] f_{s'}(r') \, dr \, dr'. \]

(9)

These quantities also appear in nonrelativistic density fitting approaches. The vector \( \mathbf{v} \) is the projection of the electrostatic potential (due to the true density) on the fitting functions,

\[ v_s = \langle f_s \| \varrho \rangle = \sum_{\mu \nu} (L^{LL}_{\mu \nu} D^{LL}_{\mu \nu} + L^{SS}_{\mu \nu} D^{SS}_{\mu \nu}), \]

(10)

which can be expressed in terms of the density matrix elements \( D^{TT}_{\mu \nu} \) and the three-center two-electron repulsion integrals

\[ I_{i,m} = \langle f_i \| \varrho^{TT} \rangle, \]

(11)

involving the auxiliary fitting functions and the \( G \)-spinor charge overlaps.\(^{21} \) The fitted element of the Coulomb interaction matrix in the Dirac–Hartree–Fock or DKS equations becomes

\[ \sum_{\mu \nu} d_s I_{i,m}^{TT} \]

(12)

The formal problem of computing the four-center two-electron repulsion integrals required for the evaluation of the Coulomb matrix is thus reduced to the calculation of the two-center and three-center two-electron repulsion integrals defining the matrices \( \mathbf{A} \) and \( \mathbf{I}^{TT} \), respectively. This reduces the formal scaling from \( \mathbf{O}(N^4) \) to \( \mathbf{O}(N^3) \) in the evaluation of the Coulomb contribution.

A specific advantage of our implementation of the Coulomb fitting described above is that we use directly primitive HGTFs as auxiliary basis functions. This permits the direct evaluation of the two-electron integrals in Eqs. (10) and (12) between HGTFs without any further computationally expensive transformation. An important simplification emerges from using sets of primitive HGTFs that have different angular momentum but identical exponent, so that to any given auxiliary function there correspond also all the functions of smaller angular momentum which have the same exponent. This scheme enables the efficient use of the recurrence relations of the Hermite polynomials in the computation of the two-electron integrals. The algorithm scales as \( \mathbf{O}(N^3) \), just as it does in the nonrelativistic case, and represents a dramatic improvement in efficiency over the conventional approach for the computation of the Coulomb matrix.

### III. POISSON FITTING AND ITS IMPLEMENTATION FOR THE DKS COULOMB PROBLEM

The basic idea of “Poisson fitting,” first discussed by Mintmire and Dunlap,\(^{35} \) and recently turned into a practical implementation by Manby et al.,\(^{16,17} \) is to exploit the Poisson equation for the Coulomb potential \( \varphi(r) \),
\( \hat{P} \rho(r) = \rho^*(r), \) 

where \( \hat{P} = -(1/4\pi)\nabla^2 \) and 

\[
u(r) = \int \frac{\rho(r')}{|r - r'|} \, dr'. \tag{14}
\]

in the evaluation of the the Coulomb energy and matrix elements. If, to represent the potential, we now adopt the fitting expansion 

\[
\bar{v}(r) = \sum_{i=1}^{N_p} \rho_i \xi_i(r) \tag{15}
\]

for a set of \( N_p \) suitable auxiliary functions \( \xi_i(r) \), then the Poisson equation gives rise to the density fitting scheme 

\[
\bar{\rho}(r) = \sum_{i=1}^{N_p} \rho_i \hat{P} \xi_i(r). \tag{16}
\]

It is easy to see how using the Poisson equation brings about a significant simplification of the Coulomb integrals in the DKS fitting procedure. A potential of the form Eq. (14) satisfying the Poisson equation clearly has the integral representation

\[
u(r) = \int \frac{\hat{P} \nu(r')}{|r - r'|} \, dr'. \tag{17}
\]

If we assume the same identity to hold for the individual components of the potential represented by the fitting functions (which implies that they fall off as \( 1/r \) for \( r \rightarrow \infty \)), then the matrix elements of the Coulomb interaction over the density fitting functions, Eq. (9), simplify as

\[
A_{ij} = \langle \xi_i | \hat{P} \xi_j \rangle = \int \xi_i(r) \hat{P} \xi_j(r) \, dr, \tag{18}
\]

reducing a six-dimensional electrostatic integral to a three-dimensional one-electron integral. Introducing the same transformation into the three-center integrals simplifies them to one-electron integrals as well,

\[
T_{k,\mu,\nu}^T = \langle \xi_k | \hat{P} \xi_\mu \rangle. \tag{19}
\]

The efficacy of this approach depends only on the accuracy with which \( \bar{v}(r) \) in Eq. (15) approximates \( v(r) \), which in turn depends on two critical considerations: the asymptotic form of \( v(r) \) and the choice of the auxiliary fitting basis functions.

In the implementation proposed by Manby et al.\(^{16, 17}\) GTFs were used to expand the Coulomb potential, thus exploiting all the further simplifications that Gaussian functions afford in the evaluation of the one-electron integrals. Obviously, the resulting approach represents a dramatic saving in computational requirements, both in terms of processing time and storage. However, with fitting functions that decay faster than any power of \( 1/r \), such as any class of Gaussian functions, the fitted potential has an unphysical asymptotic behavior: it turns out that the fitted electron density integrates to a vanishing net charge and has vanishing higher order moments, which is obviously unacceptable.\(^{16, 17}\) The correct long-range behavior of the Coulomb potential may be restored in several ways (see, for example, Refs. 18 and 20). In their original work, Manby and Knowles proposed the use of a hybrid fitting procedure, combining both the electrostatic and the Poisson metric.\(^{17}\) The total electron density is thus cast in the form

\[
\rho(r) = \sum_i d_{fi}(r) + \sum_a c_a \hat{P} \xi_a(r), \tag{20}
\]

where the \( f_i(r) \) are a (hopefully small) number of conventional basis functions, which generate the correct asymptotic behavior of the electrostatic potential and produce its correct multipole moments. The Poisson fitting functions \( \hat{P} \xi_a(r) \) are used to adjust the shape of the charge density without altering long-range characteristics of the potential. Having restored the presence of conventional basis functions in the density fitting procedure, part of the savings afforded by the Poisson procedure are of course lost, the balance depending critically on the number of conventional functions required to satisfactorily fit the density. In the nonrelativistic implementation,\(^{17}\) it has been found that this number is very small, with almost all basis functions being of the Poisson type.\(^{16, 17, 36}\) We shall now give some more details about specific aspects of the implementation of the Poisson density fitting in the context of the general methodology adopted in the relativistic four-component DFT module of the program BERTHA.

In the current implementation we choose to use directly primitive HGTFs as auxiliary basis functions. As happens in the standard density fitting approach,\(^{37, 38}\) this brings many powerful simplifications. The Poisson auxiliary functions for the density \( \hat{P} \xi_a \) are generated simply by the application of the operator \( \hat{P} \) to the HGTFs, yielding

\[
\hat{P} \xi_a = \hat{P} H[\beta; \tau, \mu, \nu; r] \tag{21}
\]

\[
= -\frac{1}{4\pi} H[\beta; \tau + 2, \mu, \nu; r] + H[\beta; \tau, \mu + 2, \nu; r] + H[\beta; \tau, \mu, \nu + 2; r], \tag{22}
\]

so \( \hat{P} \xi_a \) is simply a sum of HGTFs with larger angular momentum. The Poisson HGTF fitting basis is constructed to form groups sharing the same exponent, just as is the case in conventional fitting procedures, so that, for each given HGTF, all elements with smaller angular momentum indices are also included. This choice allows us to exploit efficiently the recurrence relations for the Hermite polynomials, not only in the two electron repulsion integrals, as discussed earlier (see also Ref. 21), but also in the one-electron integrals arising in the Poisson scheme.

Exactly as in the scheme proposed by Manby and Knowles, the separation of basis function in “standard” and “Poisson” groups induces a block structure of the Coulomb interaction. The matrix \( \mathbf{A} \) is thus partitioned as follows:

\[
\mathbf{A} = \begin{pmatrix} C & S \end{pmatrix} \begin{pmatrix} S^T & P \end{pmatrix}. \tag{23}
\]

The elements of block \( C \) are the standard Coulomb two-electron integrals over scalar auxiliary HGTFs,
The elements of block $S$ represent the Coulomb interaction between standard and Poisson functions, resulting (see below) in one-electron overlap integrals among HGTFs,

$$S_{ab} = \langle \xi_a | f_b \rangle.$$  \hspace{1cm} (25)

Finally, block $P$ represents the Coulomb interaction among Poisson functions of elements defined by

$$P_{ab} = \langle \xi_a | P \xi_b \rangle.$$  \hspace{1cm} (26)

These integrals are the standard nonrelativistic kinetic-energy-like integrals given by sums of three two-center, one-electron overlap integrals over HGTFs.

The three-index matrix $I^{TT}$ has elements coupling fitting functions and $G$-spinor pairs. It is thus also blocked as follows:

$$I^{TT} = \begin{pmatrix} I^{(s)TT} \\ I^{(p)TT} \end{pmatrix}.$$  \hspace{1cm} (27)

The upper block $I^{(s)TT}$ is made of the standard three-center two-electron repulsion integrals defined by Eq. (11). The lower block $I^{(p)TT}$ contains the integrals

$$I^{(p)TT}_{\alpha,\mu\nu} = \langle \xi_a | \tilde{P}^{TT} | \xi_b \rangle,$$  \hspace{1cm} (28)

which are simpler three-center one-electron integrals.

The main computational burdens in the fitting procedure presented above are the calculation of the vector $v$, Eq. (10), and the fitted matrix elements $\tilde{J}_{\mu\nu}^{TT}$, Eq. (12). Both these steps require the computation of the three-index matrices $I^{TT}$. These integrals may be computed efficiently, and without explicit reference to the large or small component, by adopting the same computational approaches we have described for the $J$-matrix algorithm and extensively used in the standard relativistic density fitting. The vector $v$ is also partitioned in two different sections and can be computed efficiently using the Hermite Gaussian density matrix, rather than by applying Eq. (10) directly, where the density matrix $D^{TT}$ is explicitly involved. Using the definition of the Hermite density [see Eqs. (4) and (5)], the elements of the standard upper block of the vector $v$ are

$$v_s = \sum_{\alpha} \sum_{i,j,k} H_0[\alpha; i, j, k] \langle f_i | v; i, j, k \rangle,$$  \hspace{1cm} (29)

where $\langle f_i | v; i, j, k \rangle$ are two-electron repulsion integrals over HGTFs. The elements of the lower (Poisson) block of the vector $v$ are defined by

$$v_a = \sum_{\alpha} \sum_{i,j,k} H_0[\alpha; i, j, k] \langle \xi_i | \alpha; i, j, k \rangle,$$  \hspace{1cm} (30)

where $\langle \xi_i | \alpha; i, j, k \rangle$ are simple, two-center overlap integrals over HGTFs.

Using this approach we avoid any explicit reference to the large or small components and are free to exploit all the advantages of using the Hermite density matrix that we have seen in the $J$-matrix algorithm. In similar fashion, using Eqs. (3) and (20) in Eq. (12), the fitted Coulomb matrix elements are expressed as

$$\tilde{J}_{\mu\nu}^{TT} = \sum_{i,j,k} E_0^{TT}[f_i, \nu; i, j, k] \times \left( \sum_{\alpha=1}^{N_\alpha} \langle f_i | \alpha_{\mu\nu}; i, j, k \rangle + \sum_{\alpha=1}^{N_\alpha} \langle \xi_i | \alpha_{\mu\nu}; i, j, k \rangle \right),$$  \hspace{1cm} (31)

in which the large- and small-component integrals involving fixed primary spinor basis function indices $\mu$ and $\nu$ may be evaluated simultaneously because the integrals required for the large component are a subset of those required for the small component. \(^9\) The spinor structure is entirely contained in the coefficients $E_0^{TT}$ and is completely ignored in the generation of the integrals. Using the definition of $E_0^{TT}$ and of the Hermite density, both the computations of the vector $v$ and of the fitted Coulomb matrix $\tilde{J}^{TT}$ have thus been explicitly reduced to the calculation of the simplest two-electron integrals $\langle f_i | \alpha, \beta; i, j, k \rangle$ and one-electron overlap integrals $\langle \xi_i | \alpha; i, j, k \rangle$ involving two HGTFs. The efficiency of this density fitting approach thus depends entirely on the efficiency of the computation of these basic integrals, which are the simplest analytical multicenter integrals occurring in either nonrelativistic or relativistic quantum chemistry. All the information on the relativistic nature of the interaction is contained in the coefficients $E_0^{TT}$.

IV. RESULTS AND DISCUSSION

A. Auxiliary basis set

In order to test the method we have implemented as summarized in the previous section, a suitable Poisson auxiliary basis set needs to be generated. An active literature exists dealing with the optimization of the standard density fitting auxiliary basis set that fit the total density and overlap densities in the Hartree–Fock and post Hartree–Fock methods; Refs. 39 and 40 may be consulted for the most recent studies. Information regarding the numerical details of the Poisson fitting procedure is, however, much more scarce. Manby et al.\(^{10}\) optimized the basis sets for the elements of the first row of the Periodic Table in the context of nonrelativistic DFT. A satisfactory optimization scheme was obtained using a simple three-parameter extension of the even-tempered series of exponents proposed by Eichkorn et al.\(^{12}\) It was shown that only $2s$ and $1p$ functions are required, in addition to a set of $6s3p6d1f$ Poisson functions, in order to achieve accurate fitting in the case of first row atoms C to F. The size of this basis was chosen to ensure that the error in the Coulomb energy was below 0.2 mhartree/atom, also for molecules. An extension of this optimization strategy, again applied to the first row elements, was used by Polly et al., who investigated the performance of the Poisson fitting scheme in the generation of the Fock matrix in Hartree–Fock calculations.\(^{36}\) In this case spin-orbital overlap densities were fitted.

Basis set optimization, in general, is, of course, a complicated and time consuming task, especially when large basis set with high angular momentum functions is required, as is so often the case for describing transition metals and other heavy atom systems. As is clear from the discussion in the previous section, the greatest effort must be invested in the
design of a simple and general way to construct a suitable fitting basis, which includes the minimum practicable number of conventional auxiliary functions while preserving the accuracy of a standard density fitting scheme. This strategy minimizes the number of expensive two-electron repulsion integrals that have to be calculated. There are of course many ways to approach this task but in the present work, mainly focused on an analysis of the performance of the Poisson fitting approach within our specific four-component DKS scheme, we did not really engage in an exhaustive study of this problem. We did, however, explore a number of solutions, guided in part by previous research, and found that the fitting procedure described below is particularly simple, general, and effective.

The first step of our approach consists of taking a good conventional HGTF fitting basis set optimized over the Coulomb metric, the accuracy of which fixes our accuracy target, and applying the Poisson operator to it. This generates in the simplest way an initial basis set of Poisson functions. As will be remarked shortly, further optimization or reduction of this set, given the high efficiency of the handling of the Poisson functions, brings only marginal benefits, if any at all. In the second step, we add and optimize a small number of standard fitting functions in order to achieve a prescribed fit accuracy. This is carried out as follows: we fix a small number of distinct exponent values (two or three are found to be sufficient) and their maximum associated angular momenta. For each exponent, we always include HGTFs of all angular momenta up to the specified maximum value. These functions are then added to the Poisson basis and their exponents are then optimized by calculations on some small molecules, either using a three-parameter even-tempered formula or a full optimization. Subsequently, the number of standard basis functions are progressively reduced, simply by reducing their maximum momentum starting with the functions of highest exponent. At this stage the exponents may be reoptimized although we found this to be of little benefit. The basis size reduction is terminated when the accuracy of the fit decreases to the level originally provided by the standard fitting set that initialized the procedure.

Clearly, much more sophisticated optimization strategies may be envisaged and some of these have been explored by us. For instance, we considered a full reoptimization of the Poisson functions in the spirit of previous suggestions. However, such optimization procedures, also in view of their cost when large basis sets with high angular momenta are involved, improve only marginally the accuracy of the Poisson fitting. Furthermore, we found systematically that the fitting accuracy drops appreciably as soon as the number of Poisson functions is reduced, largely offsetting the small computational savings. The approach we have presented here is simple and fast and requires only the optimization of a few functions because it exploits standard, optimized fitting basis sets. As we now demonstrate, remarkably high accuracy is preserved both for light and heavy atoms.

As first example we considered the gold dimer, examining the performance of two previously optimized standard fitting basis sets, referred to as B16 (210 functions on each Au atom) and B20 (307 functions). Once these are used as Poisson basis sets, we found with the procedure described above that the addition of just two \(s\) and one \(f\) exponents (22 HGTFs) on each Au atom as standard fitting functions was sufficient to recover the level of accuracy obtained by standard fitting. In particular, the error in the total Coulomb energy of \(\text{Au}_2\) was found to be less than 0.13 and 0.008 mhartree using the B16 and B20 sets, respectively.

For a test on light atoms we considered the water molecule and a commonly used nonrelativistic density fitting basis set, denoted DGA2. We directly generated the Poisson basis functions from this without further manipulation, as described above. In this case, the accuracy delivered by conventional fitting using the DGA2 basis set (error of 0.15 mhartree in the Coulomb energy of water) is achieved by just adding one \(s\) and one \(d\) exponents on oxygen along with one \(p\) exponent on hydrogen. The \(G\)-spinor basis set for the \(\text{H}\) and \(\text{O}\) atoms used for these test calculations has been derived from the uncontracted nonrelativistic 6-31G* basis.

In the case of water we have investigated the sensitivity of the results to the optimization of the exponents of the additional standard fitting functions, in order to gain some insight into the stability of our procedure. In Fig. 1 we show the error in the fitted Coulomb energy of water as a function of the exponents of the two standard HGTF sets on oxygen, with their maximum angular momentum set at \(\ell = 0\) and \(\ell = 2\), respectively, as mentioned above. It is eye catching that the resulting error surface is very flat over a very wide range of exponent values. A random choice of the exponents leads, in any case, to an error in the energy below 0.9 mhartree. The accuracy obtained using the standard fitting procedure (0.15 mhartree) lies on the lowest contour level shown in the figure, emphasizing very clearly that a wide area of exponent choice would lead to better accuracy in the Poisson scheme. This demonstrates that the Poisson functions generated as we have described here provide a quite flexible fitting framework, the role of the additional standard functions being only that of improving the tail of the Coulomb potential, which does not depend on the details of the density but only on its multipole expansion. This observation is obviously very general and applies as well to the case of heavier atoms.
B. Accuracy

In order to test the general accuracy of both the relativistic Poisson density fitting method and of our scheme for the generation of the Poisson auxiliary basis set, we calculated some spectroscopic properties of the gold dimer and the highly polar CsAu molecule: equilibrium bond length ($R_e$), harmonic frequency ($\omega_0$), dissociation energy ($D_e$), and dipole moment. We employed the two auxiliary basis sets B16 and B20 and their Poisson extension (P-B16 and P-B20) obtained as described in the previous section. In the case of the cesium atom an identical procedure for the optimization of the fitting basis has been used. The large component of the $G$-spinor basis sets that we used is $23s18p14d8f$ on each gold atom and $23s17p10d1f$ for cesium.\textsuperscript{44} The corresponding small-component basis was generated using the restricted kinetic balance relation.\textsuperscript{28}

The density functional used is the Becke 1988 exchange functional (B88) (Ref. 45) plus the Lee-Yang-Parr correlation functional\textsuperscript{46} (BLYP). All calculations were carried out with a total energy convergence threshold of $10^{-7}$ hartree, and the equilibrium bond length was determined iteratively using a quadratic fit to the energy. The covalent dissociation energy of Au$_2$ was determined by calculating the atomic closed shell monoions (cation and anion) and employing the experimental values of the ionization potential and electron affinity of gold and cesium.\textsuperscript{47,48}

Table II shows the results of the Poisson density fitting calculations compared with standard density fitting ones, together with the results obtained using the conventional exact DKS Coulomb matrix. The results show that the performance of standard and Poisson fitting are essentially identical. In particular, and somewhat remarkably, molecular properties such as the dipole moment of CsAu are also reproduced with the same accuracy as standard fitting methods, providing a stringent test for the relativistic Poisson fitting procedure. In Table II we have also reported the errors in the computed Coulomb and total energies introduced by both fitting procedures. We note that, independent of the auxiliary

\begin{table}
\centering
\begin{tabular}{lccc}
\hline
\hline
& Standard & Poisson & \\
\hline
\multirow{3}{*}{cc-pVDZ\textsuperscript{2}} & $\Delta E_f$ (mhartree) & $\Delta E_f$ (mhartree) \\
\hline
& 0.212 & 0.085 \\
& 0.175 & 0.113 \\
& 0.198 & 0.131 \\
\hline
\end{tabular}
\caption{Accuracy in the Coulomb energy of a water molecule using the DGA2 fitting basis sets.}
\end{table}

\begin{table}
\centering
\begin{tabular}{lcccc}
\hline
& Standard & Poisson & \\
\hline
\multirow{2}{*}{B16} & $R_e$ (Å) & 2.556 & 2.556 & 2.556 \\
& $\omega_0$ (cm$^{-1}$) & 172 & 175 & 172 \\
& $D_e$ (eV) & 2.33 & 2.31 & 2.32 \\
& $\Delta E_f$ (mhartree) & 0.129 & 0.007 & 0.121 \\
& $\Delta E_{tot}$ (mhartree) & 0.103 & 0.005 & 0.099 \\
\multirow{2}{*}{Au$_2$} & $R_e$ (Å) & 2.312 & 2.312 & 2.312 \\
& $\omega_0$ (cm$^{-1}$) & 92 & 92 & 92 \\
& $D_e$ (eV) & 2.64 & 2.64 & 2.64 \\
& $\mu$ (eV) & 10.66 & 10.67 & 10.66 \\
& $\Delta E_f$ (mhartree) & 0.028 & 0.001 & 0.041 \\
& $\Delta E_{tot}$ (mhartree) & 0.029 & 0.001 & 0.042 \\
\hline
\end{tabular}
\caption{Spectroscopic constants of Au$_2$ and CsAu calculated at the DKS/BLYP level. The Coulomb energy has been computed exactly (i.e., with no density fitting) and with two different density fitting basis set (B16 and B20, described in the text). The error in the Coulomb, $E_f$, and total, $E_{tot}$, energies arising from the fitting procedure are also reported.}
\end{table}

\textsuperscript{a}References 47 and 48.
basis used, the small error in the Coulomb energy propagates to the total energy without significant amplification in both cases.

We also tested the accuracy of the method in computing energy differences in for a molecular system in which there are both heavy and light elements. As an example, the eduction energy of a water molecule from Au(H_2O)_8^+ was calculated in the Poisson-fitted representation. The geometries of the molecules involved, optimized via all-electron ZORA calculations using the program ADF, have been kept fixed for standard, Poisson, and exact Coulomb treatments. For H and O the G-spinor basis was derived by uncontracting the 6-31G* basis set and the auxiliary fitting basis set id the DGA2 basis and its Poisson extension (PDGA2), as mentioned in the previous section. The results and accuracies of the calculation are reported in Table III. As can be seen, the error due to the standard density fitting on the extraction energy is only 0.002 eV, which is further reduced to 0.001 eV in the Poisson fitting calculation.

C. Computational efficiency

To assess the computational effectiveness the Poisson density fitting approach in our implementation, its relative performance and scaling properties were evaluated by comparison with the exact J-matrix approach and with the standard density fitting scheme of our previous work. We performed restricted DKS calculations for gold clusters of various sizes: Au_2, Au_3, Au_4, Au_5. To obtain results that may be compared directly throughout the test set, we used neither integral screening techniques nor molecular symmetry in the calculations. All test calculations were carried out on one processor of an Itanium-2 HP rx2600 node. The computation times for the Coulomb matrix construction are presented in Table IV, together with the dimension of the DKS matrix and the relative error in the fitted Coulomb energy.

The results demonstrate that the Poisson fitting method scales, like standard density fitting, as the third power of the number of atoms, independent of the size of the auxiliary basis, while the cost of the conventional J-matrix approach goes nearly as N^4. In addition, it should not be overlooked that, by fitting the density, a substantial reduction of the proportionality constant of the N-dependence is achieved; a reduction by a factor of 12.4 in the case of the standard fitting and a factor of approximately 19 for Poisson fitting. This is reflected clearly in the absolute time savings. For example, in the case of the largest system, Au_4^+, using the standard fitting method and the B20 basis (which delivers practically exact results) the J-matrix computation time is less than 1.5% that of the conventional algorithm, and it is further reduced to 0.9% using the new Poisson density fit.

It is very satisfactory to note that the accuracy of the Poisson density fit, as measured by the error in the Coulomb energy per atom, is well preserved upon increasing the size of the molecular system, even though the auxiliary basis sets have been optimized for the smallest systems. In the case of smaller basis set, B16, accuracy is even better preserved in the Poisson fit than it is in the standard fit procedure.

One feature of the Poisson-fitting scheme which can very usefully be exploited (but which has not yet been made use of in our present implementation) is the sparsity of the matrices involved. This sparsity stems naturally from the spatial locality of the Coulomb potential generated by the set of Poisson fitting functions, which decay exponentially. As a consequence, many more integrals are negligibly small compared to the standard density fitting procedure. The effect can be dramatic: even in a rather compact system such as Au(H_2O)_8^+ screening the integrals at a threshold of 10^{-12} hartree results in 70% of the elements of the A matrix being discarded in the Poisson fit calculation. This fraction is only 20% in the standard density fitting. Note further that,
despite the fact that the \( A \) matrix is larger in the Poisson fit (1041 \times 1041 versus 867 \times 867 in the standard fit) the number of integrals to be evaluated is about 1.8 times smaller. In fact, the total number of integrals to be computed in the Poisson fitting calculation is about only 5\% of that of the standard fitting case.

A second, larger, example is illustrated in Fig. 2, showing a map of the nonzero (black) elements of \( A \) for a linear Au\textsubscript{16} cluster calculated with the B20 basis set. In this case, 14\% of the integrals are larger than 10\(^{-12}\) in the standard fitting calculation but only 3.4\% in the Poisson fitting calculation. Of the latter, only 13\% (or 0.44\% of the whole matrix) are normal two-electron integrals. The lower map in Fig. 2 shows clearly the locality induced on the \( A \) matrix by the Poisson approach: because the Poisson functions are ordered by atom, with reference to the partitioning in Eq. (23), one sees the upper left \( C \) block of the standard Coulomb interaction and the \( P \) submatrix made up of 16 essentially local (about five atoms wide) zones around the main diagonal. Furthermore, the coupling \( S \) between \( C \) and \( P \) also shows a diagonal, localized, structure. In total, the number of Coulomb two-electron integrals in the Poisson calculation is only 3.7\% of that required for the standard fitting calculation. Figure 3 shows very clearly that the number of integrals to be computed in the Poisson calculation, because they are almost exclusively overlaplike integrals, scales essentially linearly with the number of atoms. Analogous features are displayed by the three-index integrals of the \( I \) matrix, as is shown in Fig. 4. The number of Coulomb integrals that have to be evaluated in the Poisson fitting calculation is here about 10\% of those of the standard approach and, furthermore, the linear scaling regime is soon reached as the number of gold atoms in the linear chain increases.

V. CONCLUSIONS

We have discussed the implementation of a density fitting method for the Coulomb problem in four-component relativistic DFT, employing the Poisson equation to generate a suitable auxiliary basis set. Our approach, using relativistic \( G \)-spinors, makes efficient use of the algorithms developed...
for the relativistic generalization of the \( J \)-matrix method and takes full advantage of the use of primitive HGTFs as auxiliary functions.

The generation of a suitable Poisson basis set has been shown to be particularly simple and effective. The scheme involves primarily the application of the Laplacian operator to a standard set of fitting functions. As already known in the nonrelativistic case, only very few conventional auxiliary functions need then be added to the Poisson basis in order to recover the correct long-range behavior of the potential and to achieve high accuracy in the representation of the Coulomb matrix. The exponents of these extra functions can be selected to cover a very wide range of applications, effectively eliminating the need of any optimization on a case-by-case basis. This simple procedure is found to be very accurate for both light and heavy atom systems.

The advantages of the use of fitting methods are enormous. Our relativistic version of the Poisson fitting method scales, like the standard density fitting, as the third power of the number of atoms, independent of the size of the auxiliary basis, while the cost of the conventional \( J \)-matrix approach goes nearly as \( N^4 \). Combining the implementation of the Poisson relativistic density fitting and our simple generation of the Poisson fitting basis set, we found, in addition, that the Poisson fitting shows systematically a smaller \( N \)-dependence prefactor than the standard density fitting procedure. Remarkably, this happens in spite of the fact that the Poisson auxiliary fitting basis set is slightly larger than standard auxiliary basis sets. In the case of the series \( \text{Au}_2, \text{Au}_3, \text{Au}_4, \text{Au}_5 \), using a near-limit underlying \( G \)-spinor basis, the prefactor is about 12.4 times smaller than the standard density fitting basis set, we found, in addition, that the Poisson fitting shows systematically a smaller \( N \)-dependence prefactor than the standard density fitting procedure. Remarkably, this happens in spite of the fact that the Poisson auxiliary fitting basis set is slightly larger than standard auxiliary basis sets. In the case of the series \( \text{Au}_2, \text{Au}_3, \text{Au}_4, \text{Au}_5 \), using a near-limit underlying \( G \)-spinor basis, the prefactor is about 12.4 times smaller than the standard density fitting and about 19 times smaller in the case of the Poisson fitting. These features are all reflected directly in large absolute time savings. For example, in the case of the largest test system, \( \text{Au}_5 \), the building of the \( J \) matrix took less than 1.5% of the time of the conventional algorithm. This is further reduced to 0.6% using the new Poisson fitting. Similarly to the nonrelativistic implementation of Manby et al.,\(^{17}\) the matrices involved in the relativistic version of the Poisson fitting algorithm are found to be very sparse, owing to the exponential decay of the potential representation given by the Poisson functions. The small number the nonzero integrals involving the Poisson auxiliary functions naturally suggests the future development of linear scaling algorithms.

Further improvements to the Poisson density fitting algorithm presented here are readily envisaged. The small number of standard functions that have to be added to the Poisson fitting auxiliary set to restore the correct asymptotic Coulomb decay involves a relatively large expense because the functions introduce two- and three-electron repulsion integrals. This cost may be eliminated by subtracting from the density, at each SCF iteration, the electric multipole contributions of the true relativistic electronic density to a given order. The resulting function is approximately without multipoles and may be fitted solely with the Poisson fitting functions. An implementation of this scheme has recently been discussed in the context of periodic boundary conditions\(^{18,19}\) and has been found highly effective. Kurashige et al.\(^{20}\) recently proposed a new linear scaling method for the Coulomb problem in nonrelativistic DFT, based on the fitting of the Coulomb potential using a mixed basis set of Gaussian functions and a finite elements basis, aimed at reproducing the long-range Coulomb decay. This method represents a direct extension of the Poisson relativistic density fitting we have presented here.

Having adopted the Coulomb fitting approach to the \( J \) matrix construction, either in its standard or Poisson version, the bottleneck of the DKS calculations has moved entirely to the evaluation of the exchange-correlation contribution. But the computation of the exchange-correlation matrix may also take advantage of the density fitting procedure.\(^{37,50}\) This extension is currently being implemented in our DKS code.

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