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Electron density fitting for the Coulomb problem in relativistic density-functional theory

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A density fitting approach for the Coulomb matrix representation within the four-component formulation of relativistic density-functional theory is presented. Our implementation, which uses *G*-spinor basis sets, shares all the advantages of those found in nonrelativistic quantum chemistry. We show that very accurate Coulomb energies may be obtained using a modest number of scalar auxiliary basis functions for molecules containing heavy atoms. The efficiency of this new implementation is demonstrated in a detailed study of the spectroscopic properties of the gold dimer, and its scaling behavior has been tested by calculations of some closed-shell gold clusters $(Au_2, Au_3^+, Au_4, Au_5^+)$. The algorithm is found to scale as $O(N^3)$, just as it does in the nonrelativistic case, and represents a dramatic improvement in efficiency over the conventional approach in the calculation of the Coulomb matrix, with computation times that are reduced to less than 3% for Au_2 and up to 1% in the case of Au_5^+. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2179420]

I. INTRODUCTION

Density-functional theory (DFT) is a widely used and accurate approach to the modeling of complex electronic systems with many electrons and light atoms. The simple one-particle structure of the Kohn-Sham equations[1] lends itself to many computational economies that are unavailable to other many-body methods. In recent years, methodological improvements in this approach have dramatically increased the size and complexity of the molecular systems that can be studied. These developments have increased the efficiency of the DFT by reducing the effective order of scaling with respect to the molecular size and basis set expansion length, or by reducing the scaling prefactor.

Due to the four-center two-electron repulsion integrals the formal scaling of the construction of the Kohn-Sham matrix construction is $O(N^4)$. However, almost all modern DFT codes take advantage of density fitting procedures,[2] 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 matrix from $O(N^4)$ to $O(N^3)$ and the scaling prefactor. Another method that can reduce the formal scaling from $O(N^4)$ to $O(N^3)$ is the pseudospectral (PS) approach[3] in which the traditional analytical basis sets (the spectral representation) are combined with numerical grid basis functions to evaluate the two-electron repulsion integrals.

These scaling relations apply to calculations involving small molecules. For large systems, the number of nonzero overlap distributions in the basis set grows only linearly with the molecular system. So, using integral screening techniques the effective scaling for the computation of the four-centers two-electron repulsion integrals can be reduced to $O(N^2)$. This scaling may be made even more favorable, reaching the $O(N)$ linear scaling regime both for the Coulomb and exchange-correlation matrix. This is achieved, for example, by efficiently tracking the long-range Coulomb interaction through the continuous fast multiple method,[4] and linear scaling methods for the exact exchange contribution to the exchange correlation functionals have also been proposed.[5,6] The implementations of these sophisticated economization techniques and the availability of powerful computing platforms are primarily responsible for facilitating the *ab initio* modeling of large molecular systems within the nonrelativistic framework.

Molecules, cluster, and materials containing heavy elements have drawn considerable recent attention. In order to model systems containing heavy nuclei the methods of relativistic quantum mechanics must be adopted, to capture scalar and spin-dependent interaction that are neglected in the conventional nonrelativistic formulation of quantum chemistry. The extension of DFT within the four-component generalization of the Kohn-Sham method, which we will refer to as the Dirac-Kohn-Sham (DKS) scheme, was formulated by Rajagopal and co-workers[7,8] and Macdonald and Vosko.[9] Relativistic density-functional theories have been implemented by several groups[10–14] and at many levels of approximation. 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. Several four-component relativistic

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program packages, such as DIRAC,[15] REL4D,[16] [part of the package UTCHEM (Ref. 17)], BDF,[18] and others, include a DKS module. The DKS calculations possess 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.

Despite the increased computational burden, the relativistic four-component formulation does not introduce any new unfavorable scaling with respect to the number of particles, other than in an increase in the scaling prefactor. Most existing molecular Dirac-Kohn-Sham codes are based on conventional integral-direct strategies but they are yet to take advantage of the recent algorithmic developments extensively employed in nonrelativistic DFT, especially those that utilize density fitting procedures and multipole expansions of the electrostatic potential. The recent implementation of Nakajima and Hirao[19] of the relativistic four-component extension of the pseudospectral approach of Friesner[3] is a notable exception. The purpose of this paper is to present an efficient implementation of the density fitting approach for the Coulomb matrix computation in the four-component DKS theory. This has been implemented in the DKS module of the program BERTHA.[14,20,21] In Sec. II we briefly review the DKS method as implemented in BERTHA, with particular emphasis on the relativistic generalization of the J-matrix method that is used to construct the Coulomb matrix. In Sec. III a detailed illustration of the relativistic density fitting approach is presented. In Sec. IV we discuss the accuracy and efficiency of our approach by analyzing the results of calculations on various gold clusters. Finally, we outline some future developments of the method.

II. THEORY

The formulation of the DKS scheme implemented in the program BERTHA has been described in detail previously[14] and in the following we shall review only some aspects of the method, especially in relation to the computation of the matrix representation of the Coulomb interaction.

The DKS equation, considering only the longitudinal electrostatic interactions, is

$$\{c\alpha\cdot\mathbf{p}+\beta c^2+v^L(\mathbf{r})\}\Psi_i(\mathbf{r})=E_i\Psi_i(\mathbf{r}), \qquad (1)$$

where the diagonal potential operator $v^L(\mathbf{r})$ is given by the sum of three terms,

$$v^L(\mathbf{r})=v_{\text{ext}}(\mathbf{r})+v_H^L[\varrho(\mathbf{r})]+v_{\text{xc}}^L[\varrho(\mathbf{r})]. \qquad (2)$$

The external potential due to the fixed nuclei is denoted $v_{\text{ext}}(\mathbf{r})$, and $v_H^L[\varrho(\mathbf{r})]$ represents the electronic Coulomb interaction, which is a functional of the relativistic charge density, $\varrho(\mathbf{r})$. The term denoted $v_{\text{xc}}^L[\varrho(\mathbf{r})]$ 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 functionals may be used as a first reasonable approximation to which relativistic corrections may be added.[22,23]

To represent the four-component solutions of Eq. (1), BERTHA uses a Gaussian basis set expansion of G-spinor functions.[14] G-spinors are themselves two-component functions of spherical Gaussian type,[24] which serve as a basis for four-component molecular spinors. This basis does not suffer from the variational problems of kinetic balance[25] if a finite nuclear charge distribution is employed, and retain all the advantages regarding the evaluation of multicenter integrals that have established Gaussian-type functions as the most widely-used expansion set in quantum chemistry.

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 ($\mathbf{J}$) and exchange-correlation ($\mathbf{K}$) contributions dominate the computational cost of the calculation. The $\mathbf{J}$ and $\mathbf{K}$ matrices are composed of two diagonal blocks, corresponding to the large-large (L) and small-small (S) component interactions. The evaluation of the exchange-correlation term is carried out by numerical integration procedures.[14] In particular, multicenter integrals over functionals involving $\varrho(\mathbf{r})$ and $|\nabla\varrho(\mathbf{r})|$ are evaluated efficiently using the methods based on those described by Becke.[26] The Coulomb interaction matrix is constructed analytically using an efficient relativistic generalization of the J-matrix method of Almlöf and co-worker.[27,28] To clarify later discussion, we briefly describe this method as implemented in BERTHA; for further details see Refs. 14 and 29.

A fundamental property of the G-spinor overlap charge-density, $\varrho_{\mu\nu}^{TT}(\mathbf{r})$ (i.e., the scalar product of G-spinors μ and ν, with $T=L,S$) is that it can be expressed as a finite linear combination of scalar auxiliary functions, similar to the McMurchie-Davidson expansion of the charge density,[30]

$$\varrho_{\mu\nu}^{TT}(\mathbf{r})=\sum_{ijk}E_0^{TT}[\mu,\nu;i,j,k]H[\alpha,\beta;i,j,k;\mathbf{r}]. \qquad (3)$$

Here, $H[\alpha,\beta;i,j,k;\mathbf{r}]$ are Hermite Gaussian type functions (HGTF) in the notation of Ref. 14, with α identifying the Gaussian exponent and β the local coordinate origin determined by the application of the Gaussian product theorem to the basis functions labeled μ and ν. The E_0^{TT} coefficients, which express the entire structure of the spinor product, are described in Refs. 25, 31, and 32, and the finite limits on the summations over the indices i, j, and k are as discussed in Ref. 14. The definition and construction of the relativistic coefficients E_0^{TT} is the feature that enables the efficient analytic evaluation of all multicenter G-spinor Coulomb integrals. An explicit G-spinor representation of the total charge density, using Eq. (3), can readily be obtained as

$$\begin{aligned}\varrho(\mathbf{r})&=\sum_{T=L,S}\sum_{\mu\nu}D_{\mu\nu}^{TT}\varrho_{\mu\nu}^{TT}(\mathbf{r})\\&=\sum_{\alpha,\beta}\sum_{i,j,k}H[\alpha,\beta;i,j,k;\mathbf{r}]H_0[\alpha,\beta;i,j,k].\end{aligned} \qquad (4)$$

The coefficients $H_0[\alpha,\beta;i,j,k]$, which are the relativistic analogues of those appearing in the scalar Hermite density matrix proposed by Almlöf and co-worker,[27,28] are given by

$$H_0[\alpha,\beta;i,j,k] = \sum_{T=L,S} \sum_{\mu\nu} E_0^{TT}[\mu,\nu;i,j,k] D_{\mu\nu}^{TT}. \tag{5}$$

The matrices $\mathbf{D}^{LL}$ and $\mathbf{D}^{SS}$ are the large- and small-component density matrices, respectively.

The $\mathbf{J}$ matrix elements in terms of the G-spinor basis set and the HGTFs are given by [14,29]

$$J_{\mu\nu}^{TT} = \sum_{i,j,k} E_0^{TT}[\mu,\nu;i,j,k] \int \frac{\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} H[\alpha,\beta;i,j,k;\mathbf{r}] d\mathbf{r} d\mathbf{r}', \tag{6}$$

where, using Eq. (4),

$$\int \frac{\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} H[\alpha,\beta;i,j,k;\mathbf{r}] d\mathbf{r} d\mathbf{r}' = \sum_{\substack{\alpha',\beta' \\ i',j',k'}} \langle \alpha\beta;ijk \| \alpha'\beta';i'j'k' \rangle H_0[\alpha',\beta';i',j',k']. \tag{7}$$

This linear combination of Coulomb two-electron integrals $\langle \alpha\beta;ijk \| \alpha'\beta';i'j'k' \rangle$, involving intermediate HGTFs, are the usual ones also computed analytically in standard nonrelativistic quantum mechanics.[30] Because of the kinetic balance relation and of the definition of the E_0^{TT} coefficients, the integrals required for the large-component $\mathbf{J}$ matrix are simply a subset of the small-component ones.[20,29]

The total Coulomb energy, E_J, is then given by

$$E_J = \frac{1}{2} \sum_{\mu\nu} (D_{\mu\nu}^{LL} J_{\mu\nu}^{LL} + D_{\mu\nu}^{SS} J_{\mu\nu}^{SS}). \tag{8}$$

The J-matrix approach of Eq. (6), compared with the summation over two-electron integrals used by other four-component density-functional codes, turns out to be particularly efficient. Remarkably, its efficiency increases with increasing maximum angular momentum of the basis functions[27] and this feature is particularly important when heavy atoms are involved because of the high angular momentum of their electrons. We have recently shown that this relativistic version of the J-matrix algorithm is easily parallelized, achieving near-linear scaling with the number of processors.[20]

Despite these favorable features, the Coulomb matrix construction demands severe computational effort, compared with the nonrelativistic case, and still limits the applicability of DKS approach to small molecules. This complexity is caused by the additional degrees of freedom associated with single-particle spinor solutions of the Dirac equation (consider, for example, that the matrices are of double size and complex, and that larger basis sets are generally required) but this does not introduce any unfavorable scaling with respect to the number of atoms. It translates simply in an essentially constant multiplicative factor of computation time with respect to the nonrelativistic case.

III. RELATIVISTIC DENSITY FITTING

The use of a density fitting approach to the Coulomb problem in the nonrelativistic single-particle Kohn-Sham and Hartree-Fock theories is well established.[2,33] It is one of the main ingredients for the construction of efficient computer programs for nonrelativistic quantum chemical calculations. Furthermore, the idea is gaining momentum that additional insight about molecular properties may be extracted from the density fitting approach. An example is given by the work of Gill *et al.*,[34] where it has been suggested, by studying the properties of the expansion coefficients of the density in the auxiliary basis, that density fitting may be used for investigating locality in molecules.

The use of density fitting procedures in a four-component relativistic framework was first considered in Ref. 29. In that work, it was pointed out that standard nonrelativistic density fitting approaches may in principle be extended directly to the relativistic case with only minor adaptations, and that there is no need to introduce separate auxiliary basis sets in which to expand the large- and small-component densities, $\varrho^{LL}(\mathbf{r})$ and $\varrho^{SS}(\mathbf{r})$. Here, we extend those ideas to realize an effective computational implementation. The computational strategy that we adopt for the Coulomb density fitting approach is to use as much as possible the advantages of the algorithms developed in the J-matrix method described in the previous section and the efficient integral generation schemes that already exist in the DKS module of program BERTHA.

The total relativistic density, exactly like its nonrelativistic counterpart, is a real scalar function that can be expanded in an auxiliary atom-centered basis set, $\{f_t(\mathbf{r})\}$, according to

$$\tilde{\varrho}(\mathbf{r}) = \sum_{t=1}^{N_{\text{aux}}} d_t f_t(\mathbf{r}), \tag{9}$$

where N_{aux} is the number of auxiliary basis functions. The coefficients d_t are chosen to minimize the error of the model density $\tilde{\varrho}(\mathbf{r})$ with respect to the true density $\varrho(\mathbf{r})$. This error metric may be written as

$$\Delta = \int d\mathbf{r}_1 \int d\mathbf{r}_2 [\varrho(\mathbf{r}_1) - \tilde{\varrho}(\mathbf{r}_1)] g(r_{12}) [\varrho(\mathbf{r}_2) - \tilde{\varrho}(\mathbf{r}_2)], \tag{10}$$

where $g(r_{12})$ is a two-electron projection operator. Several schemes are available for the choice of this operator (see Ref. 34 and references therein) but, because we are approximating the J matrix, it is natural to take $g(r_{12}) = 1/r_{12}$, corresponding to the so-called Coulomb metric. This approach is the most widely used in nonrelativistic density fitting procedures and its performance has been amply documented.[2,33] It is usually called Coulomb fitting and it has the property that it variationally minimizes spurious fluctuations in the electric field.[35] An extension of the Coulomb fitting procedure based on a transformed representation derived from the Poisson equation has been proposed by Manby *et al.*[33,36]

The minimization condition of the error in Eq. (10), using the Coulomb metric requires that the projection on the fitting basis of the Coulomb potential due to the true density and that due to the fitted density are equal. This condition leads to a linear system for the vector of fitting coefficients **d**, given by

$$\mathbf{A}\mathbf{d}=\mathbf{v}, \tag{11}$$

where the real, symmetric, and positive-definite matrix **A** is the representation of the Coulomb interaction in the auxiliary basis,

$$A_{st}=\langle f_s \| f_t\rangle \equiv \int f_s(\mathbf{r})\frac{1}{|\mathbf{r}-\mathbf{r}'|}f_t(\mathbf{r}')d\mathbf{r}d\mathbf{r}'. \tag{12}$$

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

$$v_s=\langle f_s\|\varrho\rangle=\sum_{\mu\nu}(I^{LL}_{s,\mu\nu}D^{LL}_{\mu\nu}+I^{SS}_{s,\mu\nu}D^{SS}_{\mu\nu}), \tag{13}$$

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

$$I^{TT}_{s,\mu\nu}=\langle f_s\|\varrho^{TT}_{\mu\nu}\rangle \tag{14}$$

involving the auxiliary fitting functions and the G-spinor charge overlap, $\varrho^{TT}_{\mu\nu}$. The fitted total Coulomb energy may be expressed simply as

$$\tilde{E}_J=\tfrac{1}{2}\mathbf{d}^{\dagger}\mathbf{A}\mathbf{d}, \tag{15}$$

while a fitted element of the Coulomb interaction matrix in the Dirac-Hartree-Fock or Dirac-Kohn-Sham equations becomes

$$\tilde{J}^{TT}_{\mu\nu}=\langle\tilde{\varrho}\|\varrho^{TT}_{\mu\nu}\rangle=\sum_{t=1}^{N_{\mathrm{aux}}}I^{TT}_{t,\mu\nu}d_t. \tag{16}$$

The fitting problem is, except for the explicit reference to the large and the small components, identical to that of the nonrelativistic case.[2,33] The formal problem of computing the four-center two-electron repulsion integrals required for the evaluation of the Coulomb matrix is reduced to the calculation of the two-center and three-center two-electron repulsion integrals defining the matrices **A** and $\mathbf{I}^{TT}$, respectively. This reduces the formal scaling from $O(N^4)$ to $O(N^3)$ in the evaluation of the Coulomb contribution. The actual effectiveness of this approach depends, of course, on the implementation and on the number of auxiliary basis functions required to achieve an accurate fit. The matrix **A** may be computed once at the beginning of the self-consistent-field (SCF) procedure, as it does not change during the SCF cycles. Technical problems may arise because of an ill-conditioned **A** matrix. These can be circumvented by resorting to the singular value decomposition of **A**, as described in Ref. 37.

The main computational burden in the fitting procedure presented above is the calculations of the vector **v** and of the fitted matrix elements $\tilde{J}^{TT}_{\mu\nu}$. Both these steps require the computation of the three-index matrices $\mathbf{I}^{TT}$, with $T=L,S$, i.e., of three center two-electron integrals. These integrals may be computed efficiently, and without explicit references to the large or small component, by adopting some of the computational approaches we have described in the summary of the J-matrix algorithm. The vector **v** is computed efficiently using the Hermite Gaussian density matrix, rather than by applying Eq. (13) directly where the density matrix $\mathbf{D}^{TT}$ is explicitly involved. This leads to

$$v_s=\sum_{\alpha,\beta}\sum_{i,j,k}H_0[\alpha,\beta;i,j,k]\langle f_s\|\alpha,\beta;i,j,k\rangle. \tag{17}$$

This approach avoids any explicit reference to the large or small components and exploits all the advantages of using the Hermite density matrix that we have seen in the J-matrix algorithm. Analogously, using Eq. (3) in Eq. (16), we find that the fitted Coulomb matrix elements may be expressed as

$$\tilde{J}^{TT}_{\mu\nu}=\sum_{i,j,k}E^{TT}_0[\mu,\nu;i,j,k]\sum_{t=1}^{N_{\mathrm{aux}}}\langle f_t\|\alpha,\beta;i,j,k;\rangle \tag{18}$$

in which the large- and small-component integrals involving fixed primary spinor basis function indices $\{\mu,\nu\}$ may be evaluated simultaneously. The spinor structure is explicitly considered only in the definition of the coefficients E^{TT}_0, but not in the generation of the integrals, which involve only overlap charge densities. Using the definition of E^{TT}_0 and of the Hermite density, both the computation of the vector **v** and of the fitted Coulomb matrix $\tilde{\mathbf{J}}^{TT}$ have been explicitly reduced to the calculation of the two-electron integrals $\langle f_s\|\alpha,\beta;i,j,k\rangle$ between the auxiliary function f_s and the HGTFs $H[\alpha,\beta;i,j,k;\mathbf{r}]$. Thus, the efficiency of the density fitting approach depends on the efficiency of computation of these basic integrals. Since the simplest two-electron repulsion integral we may compute is that between two HGTFs, in the current implementation we choose to use directly primitive HGTFs as auxiliary basis functions. This permits the direct evaluation of two-electron integrals in Eqs. (17) and (18) between HGTFs without any further computationally expensive transformation. In nonrelativistic quantum chemistry the basis functions of choice are usually Cartesian Gaussian type functions (CGTF), since most modern quantum chemistry codes now use efficient CGTF integral generation schemes derived from the Obara-Saika algorithm.[38] From a formal point of view, however, the CGTF and HGTF bases are trivially related and span the same linear space. A further simplification arises using primitive HGTFs that are grouped together in sets sharing the same exponents. The sets are formed so that to a given auxiliary function are associated all the functions of smaller angular momentum. For instance, a d auxiliary function set contains ten primitive Hermite Gaussians, one s, three p, and six d functions all with the same exponent. This scheme allows the efficient use of the recurrence relations[24] of Hermite polynomials in the computation of two-electron integrals. Analogous schemes have been adopted in the nonrelativistic DFT code DEMON.[39]

IV. RESULTS AND DISCUSSION

A. Auxiliary basis set optimization

To test our new implementation of relativistic density fitting, it is necessary to optimize the auxiliary fitting func-

TABLE I. Recurrence parameters for the generation of density fitting function exponents for Au [Eq. (19)] and absolute deviation of the fit from the exact (GRASP) Coulomb energy of 7417.786 76 hartree (ΔE_J in millihartree).

N_{exp}	α	β	γ	ΔE_J
5	0.8939	8.6875	2.8398	1153.97
10	0.9045	2.8961	0.4352	422.25
12	0.5159	1.9998	1.9694	74.81
14	0.3131	2.3782	0.5988	5.16
16	0.1668	2.2727	0.7227	0.87
18	0.1132	2.4902	−0.0479	0.35
20	0.1148	2.4823	−0.0281	0.30

tions. In these preliminary calculations we have considered systems containing gold nuclei and have optimized the auxiliary basis functions for this heavy atom. The criteria we have used has been the same proposed by Eichkorn *et al.*[2] and Manby *et al.*,[33] who required that the total Coulomb energy is reproduced to within 0.1–0.2 mhartree/atom. Deviations of this order of magnitude should usually be of little importance for chemical applications. In order to determine auxiliary basis sets which can represent relativistic electronic charge densities within such accuracy, we followed a very simple two-step optimization procedure: (i) Optimize a basis of standard *s*-type Hermite Gaussian functions for the isolated atom. (ii) Add functions of higher angular momentum to bring the error in the molecular Coulomb energy below the required threshold.

As shown by Quiney *et al.*,[29] an accurate representation of the atomic Coulomb energy in atoms of high atomic number may be obtained using an expansion of the electronic density in a modest number of scalar *s*-type spherical Gaussian-type functions. The Gaussian exponents λ_i may be generated using a modification of the even-tempered prescription which uses three parameters, α, β, and γ, according to the recurrence relation

$$\lambda_i = \beta\left(1+\gamma\left(\frac{i-1}{N_{\text{exp}}+1}\right)^2\right)\lambda_{i-1}, \quad i=2,3,\ldots,N_{\text{exp}}, \tag{19}$$

where N_{exp} is the desired number of exponents and the recurrence is started with the seed value $\lambda_1=\alpha$. The parameters α, β, and γ may be determined by a variational procedure, approximating the atomic Coulomb energy of configuration-averaged atomic Dirac-Hartree-Fock wave functions using the program GRASP.[40,41] The results of such atomic optimization for various choices of N_{exp} are reported in Table I. The table indicates very clearly that remarkable accuracy in the atomic Coulomb energy, by the criteria mentioned above, may already be achieved with a small number of *s*-type functions. For $N_{\text{exp}}>20$, we found that the recursive procedure of Eq. (19) is affected by linear dependence in the generated set of basis functions. Quiney *et al.*[29] indicated that in heavy-element systems requiring an accurate representation of the Coulomb energy, a conventional two-parameter even-tempered scheme is to be preferred to produce spherical expansion sets for $N>20$. This was not pursued here, because in practice, for molecular calculations, we also include functions of higher angular momentum (which we shall refer to as *polarized*), which permit the reproduction of the local anisotropy of the charge density in molecular environments.

Optimizing large basis sets with high angular momenta to fit the density over the Coulomb energy is of course a complicated task and in this first work, we have not devised schemes to carry this out. Rather we wanted to begin exploring plausible solutions in order to acquire familiarity with the problem and get useful insights into the behavior of different basis sets with regard to the relations between their size, angular momentum, exponent values, and fitting quality. To begin this investigation, we took the gold dimer as our test system and adopted a crude but quite simple approach: starting from the *s*-function set optimized for the atom as described above, we initially increased the angular momentum of all functions, without changing their exponents, until ill conditioning of the **A** matrix was detected. In our procedure, an "increase" in the angular momentum of a function implies the addition of functions of sequentially higher angular momentum with an identical exponent. Subsequently, we gradually decreased the highest angular momentum, starting from the largest exponents, until the error in the Coulomb energy of Au_2 exceeded the 0.1 mhartree/atom threshold. There are of course many ways of doing this, and we examined several solutions to find a good compromise between basis set size and accuracy. To carry out this procedure, we selected just two of the *s*-type basis sets previously optimized: the B16 set which is the smallest set to reproduce the atomic Coulomb energy to within 1 mhartree (see Table I), and so appears to be an optimal starting point; and the B20 set which represents the most accurate fitting set we could handle. The B16 set was thus initially enlarged to include *g*-type functions, reaching a dimension of 560 functions, and the final set we have chosen for all subsequent calculations on the gold clusters includes 14*d* and 2*g* function sets totaling 210 functions. In the case of the B20 basis, the final set we have selected comprises 2*s*, 13*d*, and 5*g* sets (307 functions in total) and, as we shall see, delivers practically exact results in all molecular systems we have investigated. It is important to note that high angular momentum is required for functions involving large exponent values in order to achieve the target accuracy in molecular environments. Although the reasons for this requirement are yet to be investigated in detail, it may be surmised that it is related to the high angular momenta associated with the small component contributions to the density, and to the fact that HGTF sets of high ℓ (from *d* upwards) also bring with them spherically symmetrical components.

B. Accuracy of the relativistic density fitting method

To investigate the accuracy of the relativistic density fitting method we implemented, we calculated some spectroscopic properties of the gold dimer: equilibrium bond length (R_e), harmonic frequency (ω_e), and dissociation energy (D_e), employing the two different auxiliary basis set B16 and B20. The large component of the *G*-spinor basis set that we used is 23*s*18*p*14*d*8*f* on each gold atom.[42] The corresponding

TABLE II. Spectroscopic constants of the Au dimer calculated at the DKS/BLYP level. The Coulomb energy has been computed exactly and with two different density fitting basis sets. (B16 and B20). For the latter, the absolute error in the computed Coulomb and total energies are also reported.

	B16	B20	Exact	Expt.[a]
R_e(Å)	2.556	2.556	2.556	2.472
ω_e(cm^{-1})	172	175	177	191
D_e(eV)	2.33	2.31	2.31	2.36
ΔE_J (mhartree)	0.129	0.007	⋯	⋯
ΔE_{tot} (mhartree)	0.103	0.005	⋯	⋯

[a] References 45 and 46.

small component basis was generated using the restricted kinetic balance relation.[25] The density functional used is the Becke 1988 exchange functional[43] (B88) plus the Lee-Yang-Parr (LYP) correlation functional[44] (BLYP). All calculations were carried out with a total energy convergence threshold of 10^{-7} hartree, and the equilibrium bond length was determined using iteratively 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.[45,46] The same thermodynamic cycle was also used in Ref. 47. The numerical cubature for the calculation of the exchange-correlation matrix elements uses Becke's atom-centered partitioning scheme. In particular, we used atom-centered cells with a radial integration grid divided in three shells for a total of 25 336 grid points per atom.

Table II shows the results of the density fitting calculations together with the results obtained using the conventional exact DKS Coulomb matrix and the experimental reference values of the spectroscopic constants. For the equilibrium bond length of Au_2, the results in the table indicate that the fitting method essentially coincides with the exact result, independent of the auxiliary basis employed. The agreement in the other parameters is excellent as well: the error in the harmonic frequency is 5 cm^{-1} with the B16 basis and only 2 cm^{-1} with the B20 basis, while the dissociation energy is essentially exact in the latter case. In the Table II we have also reported the errors in the computed Coulomb and total energies introduced by the fitting. We note that, independent of the auxiliary basis used, the small error in the Coulomb energy propagates to the total energy without significant amplification.

C. Computational efficiency of the relativistic density fitting

To assess the computational effectiveness of our density fitting approach, its relative performance and scaling properties were evaluated by comparison with the exact J-matrix approach. We performed restricted DKS calculations for gold clusters of various sizes: Au_2, Au_3^+, Au_4, and Au_5^+. To obtain fully comparable results throughout, we used neither integral screening techniques nor molecular symmetry in the calculations. All test calculations were carried out on one processor of a Itanium-2 HP rx2600 node. The results of the timing for the Coulomb matrix construction are presented in Table III, together with the dimension of the DKS matrix and the relative error in the fitted Coulomb energy. The results demonstrate that the fitting method scales better than 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, the advantages of the fitting in terms of the reduction of the prefactor and in terms of absolute time savings are very substantial. Using the B16 basis, which exhibits adequate behavior in terms of accuracy in the energy, the calculation is more than 30 times faster than the conventional scheme for the smaller Au_2 system, and nearly two orders of magnitude faster for the pentaatomic cluster. Even using the large B20 basis, which delivers practically exact results, the J-matrix computation time is less than 1.5% of what is needed by the conventional algorithm, reducing the time required for the calculation involving the Au_5^+ cluster from nearly 7.5 h to 6.5 min. It is remarkable that such efficiency gains can be expected to be larger than those achievable in the calculation of nonrelativistic densities. This is due to the fact that the electron density of systems containing heavy atoms is relatively more localized than that of light molecules, and also to the fact that large- and small-component basis sets are required in relativistic calculations instead of the usual one-component nonrelativistic bases. It is furthermore very satisfactory to note that the accuracy of the density fit, as measured by the error in the Coulomb energy per atom, is well preserved with increasing size of the molecular system, even though the auxiliary basis sets have been optimized for the smallest system. With the B16 basis, the error in the Coulomb energy remains throughout well below the acceptable threshold,[2] barely exceeding 0.1 mhartree/atom for Au_4 and Au_5. As we said above, the limiting B20 basis delivers results essentially indistinguishable from the exact calculation.

TABLE III. Matrix size, CPU times (s), speed ratio, and accuracy (mhartree/atom) in the construction of the Coulomb matrix for various gold clusters.

			B16			B20		
Cluster	Size	Exact time	Time	Speed up	ΔE_J	Time	Speed up	ΔE_J
Au_2	1624	722	21	34	0.065	28	26	0.003
Au_3^+	2436	3567	66	54	0.095	89	40	0.003
Au_4	3248	10973	149	74	0.110	204	54	0.004
Au_5^+	4060	26571	284	94	0.126	390	68	0.007

V. CONCLUSIONS AND OUTLOOK

In this work we have presented an implementation of the density fitting approach to the solution of the Coulomb problem within the relativistic four-component Dirac-Kohn-Sham method employing *G*-spinor basis expansion. Our implementation differs only in minor details from those in common use in the nonrelativistic quantum chemistry. In particular, we have shown that there is no need to introduce distinct auxiliary basis sets in which to expand separately the large- and small-component densities. A very accurate representation of the Coulomb matrix may be obtained using a relatively modest number of scalar auxiliary basis functions with a simple choice of their exponents. We use atom-centered HGTF as auxiliary functions because this simplifies the calculation of the integrals and we can make efficient use of the algorithms already developed for the relativistic generalization of the *J*-matrix method. The density fitting approach we have implemented has no adverse impact on the efficiency of the parallel algorithm already adopted in BERTHA for the construction of the Coulomb matrix.

The method has been validated with a study of various gold clusters. For Au_2, this shows that the relativistic density fitting approach for the Coulomb energy preserves very high accuracy in the reproduction of the spectroscopic constants, with errors similar to the nonrelativistic case. The performance and scaling properties of the method have been studied by calculation of the ground state of larger clusters. The scaling of the Coulomb matrix construction is reduced, as formally expected, from $O(N^4)$ to $O(N^3)$ with respect to the number of particles. The reduction in computation time compared to the conventional four-index *J*-matrix approach is dramatic. The CPU time is reduced to a few percent in the case of Au_2 and up to about 1% for Au_5^+. The implementation of the Coulomb density fitting in the DKS formalism truly opens new perspectives of applicability of the four-component relativistic approach.

Starting from the present implementation of the Coulomb fitting method further developments can readily be envisaged, and are currently being explored by us. In our present implementation, we do not exploit the relation between the potential and the electron density defined by the Poisson equation. As recently proposed by Manby *et al.*[33,36] making use of this relation would simplify greatly the Coulomb fitting procedure, reducing the computation to mainly three-center overlap integrals instead of three-center two-electron repulsion integrals. This approach may straightforwardly be adopted within the density fitting scheme presented here.

Using the Coulomb fitting approach for the *J*-matrix construction, 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 take advantage of the density fitting procedure. This problem has not been explicitly addressed in this study, but we emphasize that the relativistic Coulomb fitting scheme we have presented here, adapts perfectly when extended to the exchange-correlation computation, as recently proposed and applied with success by Köster *et al.*[37] in nonrelativistic density-functional theory. These extensions will form the basis of our future investigations.

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