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Evaluation of the Coulomb energy in relativistic self-consistent-field theory

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Abstract. Computational schemes are presented with which to evaluate the electrostatic Coulomb energy in relativistic molecular electronic structure calculations using a basis of four-component Dirac spinor amplitudes. We demonstrate that algorithms may be constructed and implemented which differ only in minor details from those in common use in nonrelativistic quantum chemistry, and that the four-component formalism is neither as complicated nor as expensive as has been suggested recently in the literature. Spherically symmetrical atomic basis sets are presented which indicate that accurate representations of the Coulomb energy may be obtained using modest expansions of the electronic density in a scalar auxiliary basis set of spherical harmonic Gaussian-type functions.

Key words: Coulomb energy evaluation – Relativistic self-consistent-field four-component formalism – **J**-matrix method – Fitting procedures – Spherical harmonic Gaussian-type functions

1 Introduction

The calculation of the electronic structures of molecules based on the relativistic four-component Dirac formalism is widely perceived as introducing unnecessary computational complexity and expense, and has led to the development of a number of quasirelativistic approaches to relativistic quantum chemistry. These include the relativistic pseudopotential method, relativistic extensions of the semiempirical formulation, and reductions of the Dirac–Coulomb–Breit operator to two-component form. Additionally, certain variational features of the relativistic four-component formulation of the electronic problem in a finite basis set have been described recently in the literature as an "ugly problem" whose solution introduces "unwarranted" expense and "extreme programming difficulties" [1].

A closer examination of the challenges involved in constructing relativistic four-component models of electronic structure reveals that these concerns are wholly unfounded. The use of matched spinor-type basis functions is recognized as a stable and robust solution to the problem of variational collapse [2], and is used in a number of Dirac–Hartree–Fock programs, including both BERTHA [3,4] and DIRAC [5, 6], which are both under active development. These programs serve as the starting point for the evaluation of many-body corrections using relativistic formulations of many-body perturbation theory, coupled-cluster theory, multiconfigurational self-consistent-field theory, and configuration interaction. The existing relativistic four-component molecular codes are currently limited to the treatment of small molecular species. This restriction is not imposed by any intrinsic limitation inherent in the four-component formulation, but by the comparatively limited development times invested in the existing relativistic molecular codes. All existing molecular Dirac–Hartree–Fock codes are based on conventional integral direct strategies of the type pioneered by Almlöf et al. [7] which scale quadratically with the size of the system under optimal conditions, but are yet to take advantage of the recent development of linear scaling methods. These include the use of density-fitting procedures and multipole expansions of the electronic potentials. Either method is applicable directly, with minor procedural modifications, to the relativistic formulation of the electronic structure problem. The implementation of these sophisticated economization techniques and the ready availability of powerful computing platforms are primarily responsible for facilitating the ab initio modelling of large, extended molecular systems within the nonrelativistic quantum chemical framework. The most significant recent algorithmic developments in quantum chemistry have reduced the intrinsic complexity of the computational model, which is characteristic of the number of particles in the system. In contrast, the use of the relativistic four-component formulation increases

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the intrinsic complexity of the model by a fixed factor compared with the nonrelativistic Schrödinger equation, this factor being independent of the number of particles involved. This increase in complexity is caused by the internal structure of the single-particle spinor solutions of the Dirac equation, and the reduction in symmetry imposed by the spin-orbit interaction involving the electronic spin and the relativistic current density. If one is interested in modelling the structures of compounds containing heavy elements, it is these relativistic phenomena which are of the greatest interest and it seems advisable to model them as faithfully as is feasible. All quasirelativistic models aim to reproduce the results obtained from the Dirac– Coulomb–Breit operator through semiempirical means, perturbation theory, or by reduction of the spinors to two-component form. It is desirable, therefore, that no such reduction be performed if a practical implementation of the four-component formulation is feasible, both to calibrate more approximate methods, and as a computational method in its own right.

In practice, the most significant effect of employing a two-component reduction of the Dirac operator is to alter the role played by the most significant algebraic feature of the relativistic problem, the two-component operator $\boldsymbol{\sigma} \cdot \boldsymbol{p}$. In the four-component formalism, this operator couples two pairs of components, the elements of which are determined in orthogonal two-component subspaces, the spans of which are determined by the reciprocal operation of $\boldsymbol{\sigma} \cdot \boldsymbol{p}$. Matrix elements in the four-component formalism are always evaluated using a bispinor expansion in two-component functions, so that the operations are blocked into separate subspaces involving overlap products of two-component functions, which may be two component spinors or spin-orbitals. If perturbation theory or two-component reductions are employed, the operator $\boldsymbol{\sigma} \cdot \boldsymbol{p}$ appears in a series of relativistic two-component correction operators which act on a conventional spin-orbital function space. In the evaluation of the matrix elements of these relativistic correction operators, however, one must address many of the same issues that are encountered in a four-component treatment, since many of the same integrals must be evaluated over basis functions of similar functional form. In the four-component formalism, many of the economies apparently gained in the two-component formalism may be achieved simply by neglecting multicentre two-electron contributions which scale as $(Z\alpha)^4$. These contributions involve small-component overlap densities, and formally involve the most expensive classes of two-electron integral, even though their effect on the total energy and most properties is either small or negligible in most cases.

The arguments against the use of the four-component formulation are weakest if one considers the implementation of relativistic density functional theory in a form suitable for quantum chemical studies. This is particularly true for the evaluation of the Coulomb interaction energy, which is one of the most extensively studied problems in electrostatics. Electron density and the scalar electrostatic potential which is generated by it are classical quantities, and it is not significantly more difficult to construct an electron density from four-spinor amplitudes than it is to evaluate the same quantity from nonrelativistic spin-orbitals. Similarly, one may construct approximate representations of the scalar potential generated by such relativistic density distributions using precisely the same methods as one finds in nonrelativistic quantum chemistry. In this article we investigate the expansion of relativistic charge densities using scalar auxiliary basis sets of both Hermite and spherical harmonic Gaussian-type functions. The construction of the relativistic **J** matrix is described using an algorithm which is similar to that existing in nonrelativistic procedures that form the basis of several Hartree–Fock and density functional programs. This approach is extended in the present article to include the blockwise decomposition into component densities within a kinetically balanced set of *G*-spinor basis functions. The block-diagonalization of the density matrix is then described utilizing an extension of the density-fitting techniques which are a key component of integral direct approaches to the evaluation of the Coulomb energy in large, extended systems.

It is demonstrated in this article, in contrast to recent statements which advocate scalar two-component approaches to relativistic quantum chemistry [1], that computational approaches may be adopted that are both stable and practically indistinguishable from those found in existing quantum chemistry packages, and that may be implemented using straightforward extensions of existing techniques. The methods advocated here involve no difficulties which are not already present in nonrelativistic and quasirelativistic scalar or two-component formulations.

2 Evaluation of the density in a finite basis set

In a relativistic electronic quantum theory the quantities of most immediate significance are the charge density, ϱ, and the current density, $\boldsymbol{j}$, associated with a single-particle Dirac spinor, ψ. In hartree atomic units these quantities are defined by

$$\varrho = \psi^\dagger \psi \tag{1}$$

and

$$\boldsymbol{j} = c\psi^\dagger \boldsymbol{\alpha} \psi \ , \tag{2}$$

where $c\boldsymbol{\alpha} = (c\alpha_x, c\alpha_y, c\alpha_z)$ denotes the 4×4 matrix representation of the relativistic electron current operator. For the spatial part of a four-component Dirac, $\psi(\boldsymbol{r})$, we write

$$\psi(\boldsymbol{r}) = \begin{bmatrix} \psi_1(\boldsymbol{r}) \\ \psi_2(\boldsymbol{r}) \\ \psi_3(\boldsymbol{r}) \\ \psi_4(\boldsymbol{r}) \end{bmatrix} \tag{3}$$

and the corresponding adjoint vector, $\psi^\dagger(\boldsymbol{r})$, is defined by

$$\psi^\dagger(\boldsymbol{r}) = [\psi_1^*(\boldsymbol{r}) \ \psi_2^*(\boldsymbol{r}) \ \psi_3^*(\boldsymbol{r}) \ \psi_4^*(\boldsymbol{r})] \ . \tag{4}$$

The charge density and the Cartesian components of the current density are obtained by matrix multiplication using the definitions of ψ, $\psi^\dagger$, and the matrices α_q, for $q = x, y, z$. These four fundamental quantities may be assembled into a charge–current four-vector, but we make no use of such manifestly relativistic constructions here.

The principal computational task is the determination of the spinors, which are single-particle solutions of the Dirac equation constructed for some effective time-independent potential. The Rayleigh–Ritz procedure, in which the required functions are determined as finite basis set expansions, provides the foundation of most practical methods of electronic structure determination for atoms and molecules. An analysis of this method in the context of relativistic molecular structure calculations has recently been presented in Ref. [2].

Of the possible choices of basis set which we might use to expand the basis set and which do not suffer from the variational problems discussed in Ref. [2], the G-spinor basis set confers all of the advantages regarding the evaluation of multicentre integrals which make Gaussian-type functions the most widely used expansion set in quantum chemistry. The G-spinor basis set of two-component functions of the form

$$M[L,\mu,\mathbf{r}] = \frac{1}{r_{A\mu}} f_\mu^L(r_{A\mu}) \chi_{\kappa_\mu m_\mu}(\vartheta_{A\mu}, \varphi_{A\mu}) \tag{5}$$

and

$$M[S,\mu,\mathbf{r}] = \frac{i}{r_{A\mu}} f_\mu^S(r_{A\mu}) \chi_{-\kappa_\mu m_\mu}(\vartheta_{A\mu}, \varphi_{A\mu}) \ . \tag{6}$$

If we write the basis functions in the general form $M[T,\mu,\mathbf{r}]$, the label $T = L$ denotes the large component set and $T = S$ denotes the small-component set. There is a one-to-one mapping between the elements which are labelled by the multi-index, μ. This index contains information about the specification of the functions of the form

$$\mu \mapsto \{\kappa_\mu, m_\mu \lambda_\mu, \mathbf{A}_\mu\} \ , \tag{7}$$

where κ_μ is the fine-structure quantum number, $\kappa = \{\pm 1, \pm 2, \cdots\}$, m_μ is the magnetic quantum number, $-j_\mu \leq j_\mu, j_\mu = (2|\kappa_\mu| + 1)/2 \ \lambda_\mu$ is the Gaussian exponent, and $\mathbf{A}_\mu$ is the position of the local origin with respect to which the radial and angular coordinates which define the functions are specified. The functions $\chi_{\kappa_\mu m_\mu}(\vartheta_\mu, \varphi_{A\mu})$ are the two-component spin-angular functions,

$$\chi_{\kappa,m}(\theta,\varphi) = \begin{bmatrix} (\frac{j+m}{2j})^{1/2} Y_{j-1/2}^{m-1/2}(\theta,\varphi) \\ (\frac{j-m}{2j})^{1/2} Y_{j-1/2}^{m+1/2}(\theta,\varphi) \end{bmatrix} \quad \kappa < 0 \ , \tag{8}$$

$$\chi_{\kappa,m}(\theta,\varphi) = \begin{bmatrix} -(\frac{j+1-m}{2j+2})^{1/2} Y_{j+1/2}^{m-1/2}(\theta,\varphi) \\ (\frac{j+1+m}{2j+2})^{1/2} Y_{j+1/2}^{m+1/2}(\theta,\varphi) \end{bmatrix} \quad \kappa > 0 \ , \tag{9}$$

where $\ell = j + \frac{1}{2}\mathrm{sgn}\kappa$. This basis allows one to construct solutions of the central-field Dirac equation which are symmetry-adapted to the rotation double-group $SO(3)^\dagger$, reflecting all of the constants of the motion in the quantum number set $\{j, m, \kappa, a\}$.

The functional relationship between large- and small-component basis functions is determined by the kinetic balance prescription, $M[S,\mu;\mathbf{r}] \propto \boldsymbol{\sigma} \cdot \boldsymbol{p} \, M[L,\mu;\mathrm{r}]$. If we choose $f_\mu^L(r_{A\mu})$ to be the radial part of a spherical harmonic Gaussian-type function that is defined with respect to a coordinate system centred at $\mathbf{A}_\mu$, then

$$f_\mu^L(r_{A\mu}) = N_\mu^L r_{A\mu}^{l_\mu+1} \exp(-\lambda_\mu r_{A\mu}^2) \ , \tag{10}$$

and the restricted kinetically matched small component is

$$f_\mu^S(r_{A\mu}) = N_\mu^S[(\kappa_\mu + l_\mu + 1) - 2\lambda_\mu r_{A\mu}^2] r_{A\mu}^{l_\mu} \exp(-\lambda_\mu r_{A\mu}^2) \ . \tag{11}$$

The exponent set $\{\lambda_\mu; \ \mu = 1, \ldots, N\}$ is chosen in order to provide a compact representation of the spectrum, while providing as complete a representations as possible. This is the usual "basis set problem" of quantum chemistry. We shall adopt the normalization condition

$$\int M^\dagger[T,\mu,\mathbf{r}] M[T,\mu,\mathbf{r}] \mathrm{d}\mathbf{r} = 1 \tag{12}$$

for $T = L, S$. Using the standard integral

$$\int_0^\infty x^{2n} \exp(-\lambda x^2) \mathrm{d}x = \frac{\Gamma(n+1/2)}{2\lambda^{n+1/2}} \quad \lambda > 0 \ \ n = 0, 1, \ldots \tag{13}$$

and the orthonormality of the spin-angular functions, $\chi_{\kappa,j,m}$, one obtains the normalization constants

$$N_\mu^L = \left[\frac{2(2\lambda_\mu)^{l_\mu+3/2}}{\Gamma(l_\mu + 3/2)}\right]^{1/2} \tag{14}$$

and

$$N_\mu^S = \left[\frac{2(2\lambda_\mu)^{l_\mu+1/2}}{\Gamma(l_\mu + 5/2)}\right]^{1/2} \ . \tag{15}$$

It is convenient to define the normalization constant of a product density by the notation

$$N_{\mu\nu}^{TT'} = N_\mu^T N_\nu^{T'} \ . \tag{16}$$

In a G-spinor representation, any component of the four-current may be reduced to a linear combination of quantities derived from two-component objects, according to the rules

$$\begin{aligned} \varrho_{\mu\nu}^{TT}(\mathbf{r}) &= M^\dagger[T,\mu,\mathbf{r}] \sigma_0 M[T,\nu,\mathbf{r}] \\ &= \sum_{ijk} E_0[T,\mu;T,\nu;i,j,k] H[p,\mathbf{P};i,j,k] \end{aligned} \tag{17}$$

and

$$\begin{aligned} j_{q,\mu\nu}^{T\bar{T}}(\mathbf{r}) &= c \ M^\dagger[T,\mu,\mathbf{r}] \boldsymbol{\sigma}_q M[\bar{T},\nu,\mathbf{r}] \\ &= c \sum_{ijk} E_q[T,\mu;\bar{T},\nu;i,j,k] H[p,\mathbf{P};i,j,k] \ , \end{aligned} \tag{18}$$

where T is either L or S, and $\bar{T} \neq T$. The overlap components $\varrho_{\mu\nu}^{TT}(\mathbf{r})$ are the G-spinor overlap charge densities, and $j_{q,\mu\nu}^{T\bar{T}}(\mathbf{r})$ is a component of the overlap current density, where $q = \{x, y, z\}$. The expansion of these quantities, involving a finite summation over $\{i, j, k\}$ is performed using the E_q coefficients, $E_q[T, \mu; T', \nu; i, j, k]$, which we have described elsewhere [2, 3, 4], and the Hermite Gaussian auxiliary basis, $H[p, \mathbf{P}; i, j, k]$. The operators $\{\boldsymbol{\alpha}_q\}$; $q = x, y, z$ are constructed from the two-dimensional blocks $\{\boldsymbol{\sigma}_q\}$ so we are able to generate the components of the four-current without explicit consideration of zero-valued couplings between spinor components. In order to introduce additional notational symmetry, we have introduced explicitly the 2×2 unit operator $\sigma_0 = \boldsymbol{I}_2$. The definition and construction of the E_q coefficients enables the efficient analytic evaluation of all multicentre G-spinor Coulomb integrals using a relativistic generalization of the McMurchie–Davidson algorithm. In order to evaluate the matrix elements of exchange–correlation energy, however, quadrature methods are required.

3 Evaluation of the Coulomb energy using the J-matrix method

In relativistic single-particle theories it proves convenient to separate the Fock matrix into Coulomb (**J** matrix) and exchange–correlation (**K** matrix) contributions. Electron density is a real, scalar quantity, and we may eliminate all spinor structure in relativistic **J** matrix construction.

Following Almlöf [8] and Ahmadi and Almlöf [9], we define a scalar Hermite density matrix, $\mathscr{H}$,

$$\mathscr{H}[\alpha\beta; ijk] = \sum_{\mu\nu} \{E[\mu, L; \nu, L; ijk] D_{\mu\nu}^{LL} + E[\mu, S; \nu, S; ijk] D_{\mu\nu}^{SS}\} \ , \tag{19}$$

where the labels $\{\alpha\beta\}$ indicate origin locations and exponents, and the sum over $\{\mu\nu\}$ includes all basis functions of a given nominal ℓ that share the labels $\{\alpha\beta\}$. The indices $\{ijk\}$ are Hermite polynomial indices. The large-component Hermite set is a subset of the small-component set as a consequence of kinetic balance and the matching of functions. The efficiency of this approach compared with the summation over two-electron G-spinor integrals increases with increasing angular momentum, since more density is accumulated in each sum over $\{\mu\nu\}$. Although the form of $\mathscr{H}[\alpha\beta; ijk]$ is the same as the nonrelativistic case, the length is longer because $\{ijk\}$ is determined by the small component.

We employ the Hermite density to construct single-particle Coulomb matrix elements in a scalar Hermite basis set

$$[i'j'k'; \alpha'\beta' | V_C] = \sum_{\alpha\beta} \sum_{ijk} [i'j'k'; \alpha'\beta' | ijk; \alpha\beta] \mathscr{H}[\alpha\beta; ijk] \ , \tag{20}$$

where $[i'j'k'; \alpha'\beta' | ijk; \alpha\beta]$ is a two-electron electrostatic integral involving Hermite Gaussian functions.

The essential ingredients in the calculation of electrostatic Coulomb interactions in relativistic self-consistent field theory are supplied by the generalized Hermite charge–current density matrix

$$\mathscr{H}_q[\alpha\beta; ijk] = \sum_{\mu\nu} \{E_q[\mu, T_1; \nu, T_2; ijk] D_{\mu\nu}^{T_1 T_2} + E_q[\mu, T_3; \nu, T_4; ijk] D_{\mu\nu}^{T_3 T_4}\} \ , \tag{21}$$

where the charge density requires $T_1 = T_2, T_3 = T_4$, $T_1 \neq T_3$, and $q = 0$, and the components of the current density are obtained from $T_1 \neq T_2, T_3 \neq T_4, T_1 = T_4$, and $q = \{x, y, z\}$. In terms of the Hermite Gaussian functions, $H[\alpha\beta; ijk; \boldsymbol{r}]$, the electron density, $\varrho(\boldsymbol{r})$, and the components of the current density, $j_q(\boldsymbol{r})$, are given by

$$\varrho(\boldsymbol{r}) = \sum_{\alpha\beta} \sum_{ijk} H[\alpha\beta; ijk; \boldsymbol{r}] \mathscr{H}_0[\alpha\beta; ijk] \tag{22}$$

and

$$j_q(\boldsymbol{r}) = \sum_{\alpha\beta} \sum_{ijk} H[\alpha\beta; ijk; \boldsymbol{r}] \mathscr{H}_q[\alpha\beta; ijk] \ . \tag{23}$$

All spinor structure has been absorbed in the components of the charge–current density, each of which is a real, scalar quantity.

The **J**-matrix elements in the G-spinor basis set are finally obtained by repeated use of the scalar Hermite Gaussian integrals

$$J_{\mu'\nu'}^{TT} = \sum_{i'j'k'} E[\mu', T; \nu', T; i'j'k'][i'j'k'; \alpha'\beta' | V_C] \ , \tag{24}$$

where the spinor elements $\{\mu'\nu'\}$ are spanned by the scalar labels $\{\alpha'\beta'\}$, which include specification of the exponents and local coordinate origins of the spinor basis functions. This operation involves the cost of a nuclear attraction integral. The total Coulomb energy, E_J, is then given by

$$E_J = \frac{1}{2} \sum_{\mu\nu} (D_{\mu\nu}^{LL} J_{\mu\nu}^{LL} + D_{\mu\nu}^{SS} J_{\mu\nu}^{SS}) \ . \tag{25}$$

4 Evaluation of the Coulomb energy by fitting procedures

The use of density-fitting procedures is based on the observation that the set of direct products of Gaussian-type-function orbital basis functions provides a representation of the density with a high degree of redundancy. The total density is therefore fitted to an auxiliary atom-centred basis set, $\{f_t(\mathbf{r})\}$, according to the prescription [10]

$$\varrho(\mathbf{r}) \simeq \sum_{t=1}^{K} q_t f_t(\mathbf{r}) \ , \tag{26}$$

where the expansion coefficients q_t may be interpreted as representing the effective charge carried by $f_t(\mathbf{r})$. In order for this procedure to be worthwhile, the length of the expansion, K, must be proportional to the dimension of the orbital basis, N_b. Typically, the value $K = 3N_\mathrm{b}$ is regarded as a satisfactory expansion length, with respect to the compromise between accuracy of the fitting procedure and the improvement in efficiency which is sought. There are two density-fitting schemes in common use. A new scheme devised by Manby and Knowles [11] will also be discussed which fits the electrostatic potential to an auxiliary basis set, and implicitly deduces the density from it by the Poisson equation.

We emphasize that in each of these methods there is no need to introduce separate auxiliary basis sets in which to expand separately the large- and small-components densities, $\varrho^{LL}(\mathbf{r})$ and $\varrho^{SS}(\mathbf{r})$. It is also immediately apparent on physical grounds that this auxiliary basis set need be only slightly larger than the corresponding set which would be used in a nonrelativistic calculation. The use of the kinetic balance prescription requires that large- and small-component basis functions be matched in pairs, with each pair associated with a single Gaussian exponent, as defined in Eqs. (10) and (11). Consequently, the local origins of the overlap charge distributions for the large- and small-components, whose functional forms are defined by the Gaussian product theorem, are identical. This feature, which has already been exploited in the relativistic **J**-matrix algorithm, arises because the Gaussian product theorem exploits only the local origins of the basis functions and the Gaussian exponents. These quantities are in a one-to-one correspondence, so the componentwise decomposition of the overlap charge densities differs only in finite polynomial terms. In addition, the small-component density is highly localized to the neighbourhood of the nuclei. When the small-component density is summed over all occupied states the additional polynomial parts lead to a weakly anisotropic distribution dominated by one-centre basis set overlap densities densities which are readily reproduced by an atom-centred auxiliarly basis set including scalar functions involving low values of orbital angular momentum. To a first approximation, the small-component density is well-approximated by an assembly of point charges located at the positions of the nuclei. This model is sometimes used to estimate the small-component contributions to the Coulomb energy in molecular systems. In chemical applications it is known from the use of these simple models that we may readily incorporate the finite extent and aniostropy of these small-component distributions using a modest expansion of atom-centred scalar functions, so the bulk of the work in fitting the density is nonrelativistic in character.

4.1 Overlap metric

The direct fitting of the density is achieved by selecting an auxiliary basis set, $f_t(\mathbf{r})$, and constructing the overlap matrix, **S**, where

$$S_{ts} = \int f_t^*(\mathbf{r}) f_s(\mathbf{r}) \mathrm{d}\mathbf{r} = \langle f_t | f_s \rangle \tag{27}$$

If the basis functions are assumed to be elements of a column vector, **f**, an orthonormal basis $\mathbf{f}'$, may be constructed by Löwdin symmetric orthogonalization:

$$\mathbf{f}' = \mathbf{f}\mathbf{S}^{-1/2} \ . \tag{28}$$

This assumes that the overlap matrix is nonsingular, and that a solution of the matrix eigenvalue equation,

$$\mathbf{S}\mathbf{U} = \mathbf{s}\mathbf{U} \ , \tag{29}$$

may be found for the diagonal matrix **s** containing the (positive) eigenvalues of **S**. The orthogonalizing transformation is constructed according to

$$\mathbf{S}^{-1/2} = \mathbf{U}\mathbf{s}^{-1/2}\mathbf{U}^\dagger \ , \tag{30}$$

where the diagonal matrix $\mathbf{s}^{-1/2}$ has nonzero elements $[\mathbf{s}^{-1/2}]_{ii} = (s_{ii})^{-1/2}$. Clearly, difficulties will arise if the primary basis set approaches computational linear dependence, since at least one eigenvalue will approach zero. Under these circumstances, the canonical transformation is adopted in which the components corresponding to small eigenvalues are eliminated.

In the relativistic extension of this scheme, the fitted density, $\tilde{\varrho}$, is now represented by projecting it onto the orthonormal basis

$$\begin{aligned} \tilde{\varrho} &= \mathbf{f}^{\dagger\prime}\langle \mathbf{f}' | \varrho \rangle = \mathbf{f}^{\dagger\prime}(\langle \mathbf{f}' | \varrho^{LL} \rangle + \langle \mathbf{f}' | \varrho^{SS} \rangle) \\ &= \mathbf{f}^\dagger \mathbf{S}^{-1/2} \langle \mathbf{f}\mathbf{S}^{-1/2} | \varrho \rangle \\ &= \mathbf{f}^\dagger \mathbf{S}^{-1} \langle \mathbf{f} | \varrho \rangle \\ &= \mathbf{f}^\dagger \tilde{\mathbf{q}} \end{aligned} \tag{31}$$

which is just a restatement of Eq. (26) as a matrix scalar product. Note that the spinor structure of the density matrix is wholly absorbed in the definitions of the vector of expansion coefficients, **q**, each element of which may be regarded as the sum of contributions from matched pairs of large- and small-component overlap densities.

The Coulomb energy, E_J is given by

$$E_J = \tfrac{1}{2}\tilde{\mathbf{q}}^\dagger \mathbf{V} \tilde{\mathbf{q}} \ , \tag{32}$$

where

$$\tilde{\mathbf{q}} = \mathbf{S}^{-1} \langle \mathbf{f} | \varrho \rangle \ . \tag{33}$$

The Coulomb energy is a scalar quantity, and it may not as a consequence exhibit any features of the internal spinor structures from which it is constructed.

A Coulomb contribution to the Fock or Kohn–Sham matrix in a relativistic self-consistent-field calculation reflects the components to which the total electrostatic potential is coupled. A block of the Coulomb matrix is designated J_{ij}^{TT}, where $T = L$ represents the large-component block, $T = S$ represents the block constructed from the small-component overlap density, and the indices $\{i, j\}$ correspond to the spinor basis function labels. An element of $\mathbf{J}^{TT}$ is given by

$$J_{ij}^{TT} = \tilde{\mathbf{q}}_{ij}^{TT\dagger} \mathbf{V} \tilde{\mathbf{q}} \ , \tag{34}$$

where

$$\tilde{\mathbf{q}}_{ij}^{TT} = \mathbf{S}^{-1} \langle \mathbf{f} | \varrho_{ij}^{TT} \rangle \ . \tag{35}$$

The elements of the vector $\tilde{\mathbf{q}}_{ij}^{TT}$ are constructed from the integral list $\langle \mathbf{f} | \varrho_{ij}^{TT} \rangle$, which is constructed from elements of the form

$$\langle f_t|\varrho_{ij}^{TT}\rangle = \int f_t^*(\mathbf{r})\varrho_{ij}^{TT}(\mathbf{r})\mathrm{d}(\mathbf{r}) \ , \tag{36}$$

where $\varrho_{ij}^{TT}(\mathbf{r}) = M^\dagger[T,i,\mathbf{r}]M[T,j,\mathbf{r}]$. These are, in general, three-centre overlap integrals, which may be evaluated rapidly using standard methods if the primary spinor and auxiliary scalar basis sets are of Gaussian type.

4.2 Electrostatic metric

The electrostatic Coulomb integral over scalar auxiliary functions,

$$\begin{aligned} V_{ts} &= \iint f_t^*(\mathbf{r}_1)\frac{1}{r_{12}}f_s(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \\ &= (f_t|v|f_s) \ , \end{aligned} \tag{37}$$

may be used to modify the metric used to perform the fitting of the density. In this case the orthonormal basis set is

$$\mathbf{f}'' = \mathbf{f}\mathbf{V}^{-1/2} \tag{38}$$

and the fitted representation of the density, ϱ'', is

$$\varrho'' = \mathbf{f}\mathbf{Q} \ , \tag{39}$$

where

$$\begin{aligned} \mathbf{Q} &= \mathbf{V}^{-1}(\langle\mathbf{f}|v|\varrho^{LL}\rangle + \langle\mathbf{f}|v|\varrho^{SS}\rangle) \\ &= \mathbf{V}^{-1}\langle\mathbf{f}|v|\varrho\rangle. \end{aligned} \tag{40}$$

The electrostatic Coulomb energy is given by

$$E_J = \tfrac{1}{2}\mathbf{Q}^\dagger\mathbf{V}\mathbf{Q} \ . \tag{41}$$

In the relativistic extension of the scheme, a matrix element of the Coulomb interaction in the orbital basis set is

$$J_{ij}^{TT} = \mathbf{Q}_{ij}^{TT\dagger}\mathbf{V}\mathbf{Q} \ , \tag{42}$$

where

$$\mathbf{Q}_{ij}^{TT\dagger} = \mathbf{V}^{-1}(\mathbf{f}|v|\varrho_{ij}^{TT}) \ . \tag{43}$$

A typical element of the integral list $(\mathbf{f}|v|\varrho_{ij}^{TT})$ is given by

$$(f_t|v|\varrho_{ij}^{TT}) = \iint f_t^*(\mathbf{r}_1)\frac{1}{r_{12}}\varrho_{ij}^{TT}(\mathbf{r}_2)\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2 \ . \tag{44}$$

These involve three-centre, three-index Coulomb integrals which may be evaluated by standard methods, either as they are required or pretabulated in an external file. The large- and small-component integrals involving fixed primary spinor basis function indices $\{i,j\}$ may be evaluated simultaneously using almost all existing integrals generation algorithms. This feature arises because the kinetic balance prescription requires that the exponent values corresponding to labels $\{i,j\}$ are independent of the component labels, $\{T\}$.

4.3 Manby–Knowles metric

Manby and Knowles have recently proposed a scheme [11] to evaluate the Coulomb energy and Coulomb matrix elements which exploits the relationship between $v(\mathbf{r})$ and $\varrho(\mathbf{r})$ defined by the Poisson equation:

$$\nabla^2 v(\mathbf{r}) = -4\pi\varrho(\mathbf{r}) \ . \tag{45}$$

Defining $\hat{P} = -(1/4\pi)\nabla^2$, this is equivalent to $\hat{P}v(\mathbf{r}) = \varrho(\mathbf{r})$. If one constructs a fitted potential, $\tilde{v}(\mathbf{r})$, as an expansion in some auxiliary basis $\{\xi_a(\mathbf{r})\}$,

$$\tilde{v}(\mathbf{r}) = \sum_{a=1}^{K} c_a\xi_a(\mathbf{r}) \ , \tag{46}$$

the Poisson equation fixes the expansion of the density, $\tilde{\varrho}(\mathbf{r})$, to be

$$\tilde{\varrho}(\mathbf{r}) = \sum_{a=1}^{K} c_a\hat{P}\xi_a(\mathbf{r}) \ . \tag{47}$$

For any function $f(\mathbf{r})$ which decays for large $r = |\mathbf{r}|$ faster than $1/r$, an application of Green's theorem yields the identity

$$\int \mathrm{d}\mathbf{r}'\frac{\nabla^2 f(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = -4\pi f(\mathbf{r}) \ . \tag{48}$$

Noting that $\hat{P}\{\xi_a(\mathbf{r})\}$ represents the auxiliary density which generates the auxiliary potential $\xi_a(\mathbf{r})$, a matrix element of the Coulomb interaction may be written

$$J_{ab} = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \frac{[\hat{P}_1\xi_a(\mathbf{r}_1)][\hat{P}_2\xi_b(\mathbf{r}_2)]}{|\mathbf{r}_1-\mathbf{r}_2|} \ . \tag{49}$$

Application of Eq. (48) to the integration over $\mathbf{r}_1$ yields

$$J_{ab} = \int \xi_a(\mathbf{r})\hat{P}\xi_b(\mathbf{r})\mathrm{d}\mathbf{r} \ . \tag{50}$$

This reduces the six-dimensional, electrostatic two-electron integral into a three-dimensional, one-electron integral. If one considers the expansion of the density in the primary orbital basis,

$$\varrho(\mathbf{r}) = \sum_{ij}\varrho_{ij}(\mathbf{r})D_{ij} \ , \tag{51}$$

using the primary density matrix, $\mathbf{D}$, subsequent application of Eq. (48) and employing relativistic componentwise densities yields the matrix element in the mixed basis:

$$\begin{aligned} J_{a,ij}^{TT} &= \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \frac{[\hat{P}_1\xi_a(\mathbf{r}_1)]\varrho_{ij}^{TT}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|} \\ &= \int \xi_a(\mathbf{r})\varrho_{ij}^{TT}(\mathbf{r})\mathrm{d}\mathbf{r} \ . \end{aligned} \tag{52}$$

The role of the functions $\{\xi_a(\mathbf{r})\}$ is to fit the global electrostatic potential, $v(\mathbf{r})$, through the expansion defined by Eq. (46). The interpretation of Eq. (52) follows directly from the energy-density relation

$$E_J[\varrho] = \frac{1}{2}\int \varrho(\mathbf{r})v(\mathbf{r})\mathrm{d}\mathbf{r} \ . \tag{53}$$

Equations (46) and (51) may be substituted into Eq. (53) to obtain Eq. (52) without invoking the Poisson equation or Green's theorem, since no explicit functional relationship exists between $\{\varrho_{ij}(\mathbf{r})\}$ and $\{\xi_a(\mathbf{r})\}$. The efficiency of this procedure depends only on the accuracy with which $\tilde{v}(\mathbf{r})$ in Eq. (46) approximates $v(\mathbf{r})$ in Eq. (53), which in turn depends on the critical points and the asymptotic form of $v(\mathbf{r})$ and the selection of the auxiliary basis functions, $\{\xi_a(\mathbf{r})\}$.

The error in the determination of the Coulomb energy, Δ, defined by

$$\Delta = \int \mathrm{d}\mathbf{r}_1 \int \mathrm{d}\mathbf{r}_2 \frac{[\varrho(\mathbf{r}_1) - \tilde{\varrho}(\mathbf{r}_1)][\varrho(\mathbf{r}_2) - \tilde{\varrho}(\mathbf{r}_2)]}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad , \tag{54}$$

is minimized when

$$\sum_b J^{TT}_{ab} c_b = \sum_{ij} (J^{LL}_{a,ij} D^{LL}_{ij} + J^{SS}_{a,ij} D^{SS}_{ij}) \quad . \tag{55}$$

The total Coulomb energy is then of the form

$$\bar{E}_J = \tfrac{1}{2} \mathbf{V}^\dagger \mathbf{J}^{-1} \mathbf{V} \quad , \tag{56}$$

with the elements of the column vector $\mathbf{V}$ defined by

$$V_a = \sum_{ij} (J^{LL}_{a,ij} D^{LL}_{ij} + J^{SS}_{a,ij} D^{SS}_{ij}) \quad . \tag{57}$$

The elements of the square matrix $\mathbf{J}$ are defined by Eq. (50). A fitted matrix element of the Coulomb interaction in the Dirac–Hartree–Fock or Dirac–Kohn–Sham equations then becomes

$$J^{TT}_{ij} = \mathbf{V}^{TT\dagger}_{ij} \mathbf{J}^{-1} \mathbf{V} \quad , \tag{58}$$

with $J^{TT}_{a,ij}$ defining the elements of the column vector $\mathbf{V}^{TT}_{ij}$.

We may establish a more direct connection between this approach and those involving a change in the metric used to expand $\varrho(\mathbf{r})$ by putting E_J into a form analogous to Eqs. (32) and (41) by defining a column vector, $\mathscr{V}$, whose elements are

$$\mathscr{V}_a = \sum_{ij} (J^{LL}_{a,ij} D^{LL}_{ij} + J^{SS}_{a,ij} D^{SS}_{a,ij}) \quad , \tag{59}$$

the Coulomb energy may be written in the form

$$E_J = \tfrac{1}{2} \mathscr{Q}^\dagger \mathbf{J} \mathscr{Q} \quad , \tag{60}$$

where

$$\mathscr{Q} = \mathbf{J}^{-1} \mathscr{V} \quad . \tag{61}$$

The Manby–Knowles formulation selects a metric $\mathbf{J}$, which fits both the potential and the density using a single basis set, $\{\chi_a(\mathbf{r})\}$, coupling the tasks in Eq. (50) through the action of the Poisson operator, $\hat{P}$. Since the criterion which determines the quality of the fit is defined by Eq. (54). The Manby–Knowles scheme is a reformulation of the fitting scheme based on the electrostatic metric in which the auxiliary fitting basis for the density appears through a construction on the expansion of the potential.

The clear advantage of this approach is that the integrals J_{ab} are one-particle, two-centre integrals of the same general form as those involving the nonrelativistic kinetic energy operator, while the integrals $J_{a,ij}$ are three-centre, one-electron overlap integrals. Provided that the primary orbital basis functions, $\{M[T,i,r]\}$, and the auxiliary basis functions, $\{\xi_a(r)\}$, are of Gaussian type, these quantities may be evaluated analytically and rapidly. An apparent disadvantage is that the Coulomb potential due to the electrons decays as N/r for large r, where N is the number of electrons, and this behaviour will be represented poorly by a Gaussian basis set expansion. If the system is electrically neutral, however, the potential $v(\mathbf{r})$ decays exponentially beyond the classical limits of the system, provided that one includes both the nuclear and electronic charges in the definition of the complete charge density, $\varrho(\mathbf{r})$. In the evaluation of the electronic Coulomb energy, therefore, one must either restrict oneself to neutral molecules or introduce temporarily a countercharge (or distribution of charge) to render the complete charge distribution neutral at infinity. One represents the potential due to the nuclear charge (or the countercharge) in the basis set $\{\xi_a(\mathbf{r})\}$. If the nuclear charges are included, one evaluates the nuclear attraction energy and the electron repulsion energy simultaneously. In order to handle the short-range part of the nuclear Coulomb fields, the use of special basis functions,

$$\frac{f_A(\mathbf{r}) = Z_A \mathrm{erfc}(\pi|\mathbf{r} - \mathbf{A}|/2)}{|\mathbf{r} - \mathbf{A}|} \quad , \tag{62}$$

has been suggested by Manby and Knowles. They are centred at the position of each point nucleus, A, whose charge is Z_A, and whose position is $\mathbf{A}$. The corresponding coefficients of these functions in the density expansion, $\hat{P}f_A(\mathbf{r})$, in Eq. (50) are set equal to unity to satisfy exactly the Coulomb singularities. On the other hand, if one includes a single arbitrary countercharge in order to impose electrical neutrality on the fitted system, its effects may be eliminated by evaluating a simple counterterm in the form of a conventional nuclear attraction integral.

5 Results

In order to determine auxiliary basis sets which are able to represent relativistic electronic charge densities to a high accuracy, we generated average configuration atomic Dirac–Hartree–Fock wave functions using GRASP [12, 13]. The atomic electron density is spherically symmetrical and can be represented by an expansion in a scalar basis set of s-type spherical harmonic Gaussian-type functions. The explicit form of the auxiliary basis functions, $\{f_i\}$, used in this study is

$$f_i(\mathbf{r}) = N_i \exp(\lambda r^2) Y^0_0(\vartheta, \varphi) \quad , \tag{63}$$

where $\{\lambda_i\}$ $i = 1, N_{\mathrm{aux}}$ is a set of Gaussian exponents of dimension N_{aux} to be determined by a variational procedure and $Y^0_0(\vartheta, \varphi) = (1/4\pi)^{1/2}$. Although the spherical harmonic factor is trivial in this case, we include it in anticipation of future studies in which environmental polarization of the atomic charge density is included in the form of the auxiliary expansion set.

The radial spinor amplitudes generated by GRASP were tabulated on a radial grid, on which we constructed an interpolated representation of the electron density using B-splines. This was used to evaluate the required radial integrals $\langle f_i | \varrho \rangle$ using adaptive numerical quadrature. We investigated in detail the expansion of the density using the electrostatic metric, since this is known to give results which are superior to those obtained using the overlap metric in nonrelativistic studies. The determination of the set $\{\lambda_i\}$ is based on the maximization of E_J in Eq. (41). This is equivalent to the minimization of the error in the coulomb energy,

$$\Delta E_J = E_J^0 - E_J \ , \tag{64}$$

because E_J^0 is a rigorous upper bound to E_J. Note that this property merely assumes that $\varrho(r)$ is constructed from the sum over orthonormal, occupied single-particle functions representing a square-integrable N-electron density, a requirement which is satisfied equally well by both the nonrelativistic and the relativistic versions of the procedure. The boundedness of the variational procedure is a consequence solely of the laws of electrostatics and, apart from the preceding restriction, is independent of the procedure used to generate the density.

The exponent sets were generated using a modification of the even-tempered prescription, and are defined by three parameters, $\{\alpha, \beta, \gamma\}$, whose values are determined by the variational procedure. The exponent values are defined using the recurrence relation

$$\lambda_i = \beta \left[1 + \gamma \left(\frac{i-1}{N_{\text{aux}} + 1} \right)^2 \right] \lambda_{i-1}, \quad i = 2, 3, \ldots, N_{\text{aux}} \tag{65}$$

starting with the seed value $\lambda_1 = \alpha$.

Table 1. Values of the α, β, and γ parameters for different numbers of fit functions, N_{aux}, determined for the first-row elements. The fitted and finite-difference values of the Coulomb energy are given in hartree atomic units

	N_{aux}	α	β	γ	Fitted Coulomb energy	Coulomb energy
H	6	0.2012	2.2080	2.6669	0.312506122	0.312506128
	10	0.0883	2.0020	0.4865	0.312506128	
	15	0.0820	1.9972	0.1388	0.312506128	
He	6	0.4616	2.4051	2.0699	2.05166385	2.05166394
	10	0.3333	2.0427	1.0157	2.05166394	
	15	0.1001	1.9997	1.0010	2.05166394	
Li	6	0.0939	3.3748	0.5352	4.06263733	4.06268466
	10	0.0658	2.1228	1.0635	4.06268450	
	15	0.0588	2.0103	0.0939	4.06268466	
Be	6	0.1756	3.1345	0.9192	7.15778772	7.15788871
	10	0.1166	2.1904	0.8561	7.15788847	
	15	0.0760	1.9997	0.0906	7.15788871	
B	6	0.2516	3.1277	0.9296	11.5867658	11.5869516
	10	0.1496	2.3278	0.5257	11.5869511	
	15	0.0954	2.0139	0.0735	11.5869516	
C	6	0.3406	3.1676	0.8415	17.7351828	17.7354720
	10	0.1877	2.3440	0.5580	17.7354710	
	15	0.1284	2.0235	0.0834	17.7354720	
N	6	0.4506	3.1922	0.7753	25.9755716	25.9759749
	10	0.2421	2.3352	0.5735	25.9759736	
	15	0.1704	2.0379	0.0598	25.9759749	
O	6	0.5704	3.2351	0.6773	36.5684650	36.5690134
	10	0.2992	2.3321	0.5751	36.5690116	
	15	0.2177	2.0309	0.0738	36.5690134	
F	6	0.5478	2.6869	2.4399	49.8945358	49.8952449
	10	0.3673	2.3281	0.5756	49.8952425	
	15	0.2620	2.0398	0.0498	49.8952448	
Ne	6	0.6500	2.7006	2.4399	66.2089025	66.2097573
	10	0.4387	2.3206	0.5954	66.2097542	
	15	0.3190	2.0335	0.0727	66.2097572	

6 Discussion

For the elements from H to Ne, (Table 1), density fits were obtained which were judged to be good, very good, or excellent. The most approximate fits involved an expansion of six s-type functions, and reproduced the atomic Coulomb energy to millihartree accuracy, or better. Increasing the expansion length to ten s-type functions improved the accuracy of the fitted Coulomb energy to 1×10^{-5} hartree, and an expansion of 15 functions reproduced the Coulomb energy to 1×10^{-5} hartree, which is at the level of the accuracy to which the original spinor amplitudes are obtained by GRASP using the default operational parameters. For each of the 6-,10- and 15-membered sets, smooth variation was found in the parameter set $\{\alpha, \beta, \gamma\}$ as the nuclear charge was increased. As the dimension of the set was increased, there was a strong tendency for the parameter γ to decrease in value. This is in keeping with the mathematical result that an even-tempered set of Gaussian-type functions, constructed by setting $\gamma = 0$, tends towards completeness as $N_{\text{aux}} \to \infty$ provided that $\alpha \to 0$, $\beta \to 1$, and $\beta^{N_{\text{aux}}} \to \infty$. Certainly, the optimization procedure naturally returns values of α and β which tend towards the correct limiting values, and will satisfy the additional requirement $\lim_{N_{\text{aux}}} \to \infty$, $\beta^{N_{\text{aux}}} \to \infty$ provided that $\lim\ _{N_{\text{aux}}} \to \infty\ \gamma \to 0$, because this is a feature of the conventional even-tempered series of Gaussian-type functions. For these first-row elements, the auxiliary basis set is effectively saturated, and the redundancy of the parameter γ becomes increasingly apparent in the practical limit $N_{\text{aux}} \to \infty$.

A pattern similar to that found for the first-row elements is observed for the elements from Na to Ar (Table 2), except that the numerical accuracy of the fit is uniformly degraded. A larger expansion is required in order to obtain millihartree accuracy, and an expansion of 15 functions is required in order to secure fitted Coulomb energies at better than microhartree accuracy. This behaviour persists in our fitted expansions of the Coulomb potential for the second-period elements K-Kr (Table 3), and the first-row transition-metal elements, Sc-Zn (Table 4), an expansion of 18 s-type functions being able to reproduce the atomic Coulomb energy to an accuracy of 10^{-5}.

On examining the behaviour of the optimized auxiliary sets down the group C-Pb (Table 5), the accuracy is

Table 2. Values of the α, β, and γ parameters for different numbers of fit functions, N_{aux}, determined for the second-row elements. The fitted and finite-difference values of the Coulomb energy are given in hartree atomic units

	N_{aux}	α	β	γ	Fitted Coulomb energy	Coulomb energy
Na	8	0.1113	3.2019	0.3669	80.1302077	80.1312482
	12	0.0700	2.3715	0.3502	80.1312399	
	15	0.0581	2.0540	0.4521	80.1312480	
Mg	8	0.1564	3.0462	0.5267	95.9529949	95.9541530
	12	0.1026	2.3217	0.3929	95.9541451	
	15	0.0848	2.0468	0.4023	95.9541528	
Al	8	0.1781	3.0450	0.5123	113.011944	113.013535
	12	0.0991	2.2389	0.6089	113.013521	
	15	0.0775	2.1398	0.1918	113.013535	
Si	8	0.2205	2.9886	0.5661	132.131863	132.133695
	12	0.1246	2.1932	0.6867	132.133679	
	15	0.1016	2.1448	0.1116	132.133694	
P	8	0.2769	2.9167	0.6443	153.522702	153.524712
	12	0.1606	2.1497	0.7562	153.524695	
	15	0.1245	1.9645	0.6020	153.524711	
S	8	0.3376	2.8658	0.6996	177.232981	177.235195
	12	0.1973	2.1146	0.8171	177.235177	
	15	0.1629	2.0471	0.3096	177.235194	
Cl	8	0.4060	2.8221	0.7475	203.483593	203.486008
	12	0.2394	2.0816	0.8777	203.485988	
	15	0.1982	2.0331	0.3173	203.486007	
Ar	8	0.4779	2.7939	0.7758	232.340728	232.343363
	12	0.2831	2.0560	0.9258	232.343341	
	15	0.2355	2.0103	0.3577	232.343362	

Table 3. Values of the α, β, and γ parameters for different numbers of fit functions, N_{aux}, determined for the third-row elements. The fitted and finite-difference values of the Colulomb energy are given in hartree atomic units

	N_{aux}	α	β	γ	Fitted Coulomb energy	Coulomb energy
K	10	0.0146	3.8411	0.4175	258.235504	258.236411
	15	0.0537	2.0757	0.5059	258.236395	
	17	0.0489	2.0735	0.1578	258.236408	
	18	0.0473	2.0660	0.0038	258.236409	
Ca	10	0.0227	3.6203	0.4196	286.046703	286.047703
	15	0.0719	2.0250	0.5750	286.047688	
	17	0.0661	2.0371	0.0811	286.047700	
	18	0.0646	2.0204	0.1046	286.047701	
Ga	10	0.1477	2.8971	1.7741	840.778137	840.779418
	15	0.1277	2.1994	0.1729	840.779308	
	17	0.1032	2.0248	0.2794	840.779395	
	18	0.0977	2.0350	0.1056	840.779406	
Ge	10	0.1771	2.8134	1.9631	903.454214	903.455604
	15	0.1458	2.1787	0.2048	903.455495	
	17	0.1201	2.0045	0.3158	903.455583	
	18	0.1140	2.0169	0.1351	903.455593	
As	10	0.2176	2.7090	2.2244	969.013181	969.014679
	15	0.1736	2.1427	0.2645	969.014580	
	17	0.1363	2.0050	0.2744	969.014659	
	18	0.1340	2.0058	0.1139	969.014669	
Se	10	0.1159	3.4726	0.1016	1037.37578	1037.37720
	15	0.2020	2.1140	0.3123	1037.37711	
	17	0.1856	2.0777	0.0187	1037.37717	
	18	0.1622	1.9633	0.2372	1037.37720	
Br	10	0.1381	3.3894	0.1673	1108.79767	1108.79903
	15	0.2339	2.0854	0.3622	1108.79894	
	17	0.2168	2.0730	0.0468	1108.79900	
	18	0.1900	1.9413	0.2668	1108.79902	
Kr	10	0.1645	3.3038	0.2518	1183.21050	1183.21184
	15	0.2661	2.0621	0.4028	1183.21175	
	17	0.2433	2.0682	0.0194	1183.21181	
	18	0.2152	1.9270	0.3091	1183.21183	

seen to decrease steadily as the nuclear charge is increased, but remains acceptable for Pb for an expansion length of less than 20 s-type functions. In the case of Pb, we found that allowing nonzero values of the parameter γ in the generation of the Gaussian parameter set causes the auxiliary basis set to suffer from computational linear dependence for $N_{\mathrm{aux}} > 20$, so a conventional two-parameter, even-tempered set involving only α and β is preferred if larger spherical expansions are required. This was not pursued further here, because in practice one must include polarization functions in molecular calculations involving $l > 0$ to reproduce the local anisotropy of the charge density in molecular environments. These additional polarized functions are best determined by fitting the density to representative molecular hydrides or to atoms perturbed by the field of point charges, and will form the subject of future investigations.

The significant feature of the numerical results obtained here is that they are similar in character to those which are obtained if the same optimization procedure is applied to the determination of nonrelativistic fitting parameters. The variation of the parameters across a row of the periodic table is smooth and regular, and tends towards a complete set of even-tempered functions as the dimension of the fitting set is expanded. The accuracy of the fit is a smooth function of the dimension of the auxiliary set and of the nuclear charge, so reliable representations of the Coulomb energy may be obtained using the electrostatically weighted fitting metric. The accuracy of the fit down a group of the periodic table tends to decrease, and requires larger exponents and expansions of larger dimension to achieve a given accuracy; however, this rather mild increase in computational requirements must be offset against the rapid increase in cost if no fitting procedure is adopted in relativistic calculations. As the nuclear charge is increased, the need to include f-type functions in the large-component space is aggravated by the basis set matching procedure, which introduces an equal number of g-type functions in the small-component spinor space. The multicentre Coulomb integrals, even when evaluated using the J-matrix method, rapidly increase in both number and cost, but when summed over occupied spinors, the density, and in particular the contribution to the density from the small-component functions, is well-approximated by a weakly anisotropic function. This essentially classical function ought not to be constructed term-by-term from spinor overlap densities if it can be avoided, because the internal spinor structure is

Table 4. Values of the α, β, and γ parameters for different numbers of fit functions, N_{aux}, determined for the first-row transition-metal elements. The fitted and finite-difference values of the Colulomb energy are given in hartree atomic units

	N_{aux}	α	β	γ	Fitted Coulomb energy	Coulomb energy
Sc	10	0.1281	2.5352	0.8932	319.794704	319.797491
	12	0.0961	2.2368	0.7408	319.797052	
	15	0.0810	2.0232	0.5664	319.797473	
	17	0.0744	2.0223	0.2216	319.797487	
	18	0.0721	2.0192	0.0703	319.797489	
Ti	10	0.1399	2.5503	0.8800	356.745371	356.748283
	12	0.1053	2.2454	0.7153	356.747795	
	15	0.0895	2.0288	0.5430	356.748262	
	17	0.0819	2.0305	0.1895	356.748279	
	18	0.0790	2.0236	0.0419	356.748280	
V	10	0.0350	3.5832	0.3366	397.163834	397.164689
	12	0.1134	2.2613	0.6788	397.164148	
	15	0.0969	2.0393	0.5107	397.164664	
	17	0.0890	2.0443	0.1500	397.164683	
	18	0.0796	1.9847	0.0977	397.164686	
Cr	10	0.0483	3.3001	1.0938	444.938978	444.939903
	12	0.1195	2.2846	0.6348	444.939286	
	15	0.0982	2.0719	0.4413	444.939870	
	17	0.0887	2.0869	0.0592	444.939894	
	18	0.0777	1.9294	0.3496	444.939900	
Mn	10	0.0579	3.2456	1.1311	488.033859	488.034849
	12	0.1293	2.2946	0.6096	488.034197	
	15	0.1120	2.0617	0.4505	488.034815	
	17	0.1029	2.0713	0.0812	488.034840	
	18	0.0907	1.9167	0.3654	488.034847	
Fe	10	0.0481	3.5882	0.2685	538.815431	538.816381
	12	0.1373	2.3117	0.5769	538.815669	
	15	0.1193	2.0734	0.4220	538.816342	
	17	0.1101	2.0824	0.0590	538.816370	
	18	0.0960	1.9288	0.3319	538.816378	
Co	10	0.0541	3.5641	0.3063	593.366364	593.367407
	12	0.1451	2.3288	0.5447	593.366633	
	15	0.1268	2.0855	0.3930	593.367363	
	17	0.1170	2.0947	0.0253	593.367394	
	18	0.0903	2.0135	0.0648	593.367401	
Ni	10	0.0573	3.6114	0.1772	651.695754	651.696921
	12	0.1532	2.3449	0.5166	651.696081	
	15	0.1344	2.0963	0.3681	651.696871	
	17	0.1249	2.1036	0.0372	651.696905	
	18	0.1079	1.9470	0.2918	651.696917	
Cu	10	0.1048	3.0454	1.4728	720.751243	720.752319
	12	0.1598	2.3645	0.4851	720.751367	
	15	0.1334	2.1295	0.3064	720.752255	
	17	0.0860	2.0740	0.1032	720.752298	
	18	0.0931	2.0353	0.0558	720.752312	
Zn	10	0.1541	2.7775	2.1513	780.732514	780.733744
	12	0.1689	2.3778	0.4613	780.732763	
	15	0.1493	2.1188	0.3203	780.733679	
	17	0.1396	2.1305	0.0213	780.733721	
	18	0.0969	2.0544	0.0073	780.733734	

smeared out in the averaging process which generates the density. The use of fitting functions, even involving a larger expansion than would be required in a corresponding nonrelativistic study of the same system, represents a huge computational saving compared with the brute force evaluation of the Coulomb energy.

Table 5. Values of the α, β, and γ parameters for different numbers of fit functions, N_{aux}, determined for the group IV elements. The fitted and finite-difference values of the Colulomb energy are given in hartree atomic units

	N_{aux}	α	β	γ	Fitted Coulomb energy	Coulomb energy
C	6	0.3406	3.1676	0.8415	17.7351828	17.7354720
	10	0.1877	2.3440	0.5580	17.7354710	
	15	0.1284	2.0235	0.0834	17.7354720	
Si	8	0.2205	2.9886	0.5661	132.131863	132.133695
	12	0.1246	2.1932	0.6867	132.133679	
	15	0.1016	2.1448	0.1116	132.133694	
Ge	10	0.1771	2.8134	1.9631	903.454214	903.455604
	15	0.1458	2.1787	0.2048	903.455495	
	17	0.1201	2.0045	0.3158	903.455583	
	18	0.1140	2.0169	0.1351	903.455593	
Sn	12	0.1604	2.4526	1.1310	2478.36176	2478.36354
	14	0.0417	2.7129	0.2829	2478.36288	
	17	0.1519	1.9639	0.4639	2478.36307	
	19	0.1353	1.9922	0.1223	2478.36339	
Pb	14	0.2484	2.0937	1.2789	8073.62810	8073.64600
	15	0.2001	2.2314	0.7995	8073.64182	
	17	0.1491	2.4102	0.1651	8073.64528	
	18	0.0617	2.4098	0.1299	8073.64541	

7 Conclusion

The formulation of the relativistic molecular electronic structure problem using kinetically balanced sets of Gaussian-type functions immediately suggests the extension of several existing computational techniques in nonrelativistic quantum chemistry. These include the use of **J**-matrix methods to evaluate the Coulomb energy exactly within a common scalar Hermite Gaussian-type-function basis set for both the large- and small-component densities, and the use of atom-centered auxiliary basis sets to fit the density, summed over both large- and small-component contributions, using suitably chosen basis set parameters determined by variational calculations of smaller model problems, such as free atoms, atoms perturbed by effective ligand fields, or small molecular species such as hydrides. Not considered in the present study are multipole expansions of the potential, the extension of which to the relativistic framework presents no difficulties since the component charge densities are classical entities, and the small-component density is a structure which is localized to the positions of the constituent nuclei.

In the construction of the Coulomb energy or finite-dimensional representations of the Coulomb or exchange operators, the main unavoidable disadvantage of the four-component formulation is that such matrix representations are necessarily larger than their nonrelativistic counterparts, and they may be intrinsically complex for some symmetry types. The cost of matrix diagonalization is not, however, the part of a mean-field calculation which places a limit on the size of the system that can be studied. It is the cost of constructing that representation and the evaluation of the Coulomb and exchange–correlation contributions which dominate the computational budget of the calculation. In a four-component calculation these operations are always evaluated within two-component subspaces, obviating the algorithmic need to reduce the four-component Dirac operator into an effective two-component form: the algorithm is already in two-component form, and the four-component structure is restored at each matrix diagonalization. From a computational point of view, a four-component calculation involves the construction of a small number of two-component representations, and many of the effective operators which are encountered in the two-component formalism introduce operations that are procedurally equivalent to the evaluation of Coulomb or exchange–correlation matrix elements over functions generated by kinetic balance.

No significant problem exists with the use of kinetically balanced sets of *G*-spinor functions in the solution of matrix representations of the Dirac equation. It is certainly the case that small variational bounds failures may be encountered of the order $(Z/c)^4$, but these are indicative only of basis set incompleteness and do not affect the quality of bound-state solutions in any significant way. If fitting procedures are introduced in order to evaluate the Coulomb energy, or numerical grids are used to evaluate matrix elements of the exchange–correlation potential, strict variational bounding of the energy is abandoned even in the nonrelativistic model of quantum chemistry. The intrinsic uncertainties in the energy introduced by these procedures are both larger and generally of greater chemical significance than the small variational failures caused by the use of incomplete kinetically balanced sets, whose shortcomings are contained almost entirely within the representation of chemically inert core orbitals.

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