A Quasirelativistic Two-component Density Functional and Hartree-Fock Program

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This work describes the implementation of an efficient two-component quasirelativistic density functional and Hartree-Fock program. The fact that the basis functions are real can be exploited if a special internal representation of operators and density matrices is used. This also leads to a considerable reduction of the effort in the closed shell case. While in most applications to open shell molecules, the noncollinear approach to define a relativistic spin density is preferable, the collinear approach finds its application in the calculation of magnetic anisotropy energies. Linear algebra steps in the SCF procedure have a higher relative weight compared to the nonrelativistic case, therefore some care was necessary to make them fast when parallelizing the code. The quasirelativistic Hamiltonians that have been implemented are the 'zeroth-order regular approximation' (ZORA) Hamiltonian, the Douglas-Kroll-Hess Hamiltonian up to the sixth order, together with an accurate approximation to treat the picture change effect of the electron interaction, and effective core potential (ECP) matrix elements. Geometry gradients are available for the ZORA and ECP methods.

1. Introduction

The Schrödinger equation describes a nonrelativistic world as its classical limit corresponds to Newtonian mechanics. In classical physics, this is appropriate as long as the relative velocities of the particles are small compared to the speed of light, or, in other words, the kinetic energy of a particle is small compared to its rest energy mc^2. It is easily seen that this condition is not fulfilled for electrons moving in the potential of heavy (highly charged) nuclei, and since the mid-1970s it is also clear that this does not only affect electrons in the inner cores of heavy elements, but has an impact on the chemical (valence shell) properties of

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these elements [1,2]. During the 1990s, almost all molecular electronic structure codes have been extended to take relativistic effects into account, since otherwise applications to heavy-element chemistry would have remained rather limited. For a small review of this period, the reader is referred to Ref. [3]. However, most implementations have focused on so-called scalar relativistic approximations which neglect the spin-orbit interaction. Without the spin-orbit interaction, the quasirelativistic Hamiltonian has the same symmetry properties as in the nonrelativistic case. Therefore, adding scalar relativitiy to a nonrelativistic quantum chemical code is not particularly difficult, a modification of the one-electron integrals is sufficient in most cases, and most quantum chemistry codes have been extended along these lines.

For most molecules, in particular *closed shell* molecules, spin-orbit coupling has only a small effect on valence ground-state properties like bond lengths and vibrational frequencies. Excitation energies on the other hand are much more affected, especially if the spin-orbit interaction splits states which are (nearly) degenerate in a scalar-relativistic description. A standard method used in such situations is spin-orbit CI starting with relatively few highly correlated wave functions from a scalar-relativistic calculation and adding a spin-orbit configuration interaction calculation in this space [4–9]. To investigate spin-orbit effects for most molecular ground-state properties spin-orbit CI is however less suitable, and one should include the spin-orbit interaction already in the orbital optimization procedure. This not only takes care of higher-order spin-orbit effects such as orbital relaxation (atomic $2p_{1/2}$ and $2p_{3/2}$ orbitals may have quite different radial parts) but also includes spin-orbit effects in a single-configuration description that is inherent in the density functional methodology. The drawback of such an approach is that the orbitals are no longer spin eigenfunctions (either *spin up* or *spin down*) and can no longer be chosen real, such that they form complex two-component quantities. Although this is a more technical rather than a conceptual problem, it means that an existing quantum chemical computer code cannot simply be extended to run with two-component orbitals but requires a major re-design. During the past years, a number of groups have developed density functional codes with two-component spinors [10–16]. There are older two-component Hartree-Fock implementations [17,18] which seemingly have never been applied to molecules with more than a few atoms. A more recent implementation of two-component Hartree-Fock [19,20] is mainly used to generate two-component spinors for a subsequent electron correlation treatment as this implementation is restricted to the *closed shell* case.

In this article we report our implementation of the two-component computational method which differs from other implementations we are aware of, and which offers some advantages in terms of storage and number of floating point operations needed as well as an easier interface to existing non-relativistic or scalar relativistic computer code. It is shortly discussed how to define a 'spin density' in a relativistic description. The next sections give some notes on the

performance and the parallelization of the code and on the quasirelativistic Hamiltonians we are currently using.

2. Program structure

Since the Kohn-Sham density functional and Hartree-Fock method are essentially the same from the viewpoint of a computer implementation, we will treat both cases together. For an n-electron system, one starts from a single Slater determinant (either the Hartree-Fock wave function itself of the Kohn-Sham reference wave function)

$$\Psi = |\psi_1\psi_2\ldots\psi_n| \tag{1}$$

built from two-component complex molecular spinors (orbitals)

$$\psi_i = \begin{pmatrix} \phi_i^{(\alpha)} \\ \phi_i^{(\beta)} \end{pmatrix} \tag{2}$$

The basis set used to expand the scalar functions ϕ_i^α, ϕ_i^β consists of N conventional (real and scalar) Gaussian basis functions B_μ. Formally, this makes a basis of $2N$ real but two-component basis functions to expand the molecular spinors

$$\psi_i = \sum_{\mu=1}^{N} C_{\mu i}^{(\alpha)} \begin{pmatrix} B_\mu \\ 0 \end{pmatrix} + \sum_{\mu=1}^{N} C_{\mu i}^{(\beta)} \begin{pmatrix} 0 \\ B_\mu \end{pmatrix} \tag{3}$$

We will make use of the fact that our $2N$ two-component basis functions are real and eigenfunctions of σ_z, the third of the Pauli spin matrices

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{4}$$

The matrix representation $\mathbf{H}$ of a one-particle operator such as the one-electron part of the Hamiltonian $\hat{h}$ is a complex $2N \times 2N$ matrix which can be written in terms of four complex $N \times N$ blocks

$$\mathbf{H} = \begin{pmatrix} \mathbf{H}^{(\alpha\alpha)} & \mathbf{H}^{(\alpha\beta)} \\ \mathbf{H}^{(\beta\alpha)} & \mathbf{H}^{(\beta\beta)} \end{pmatrix} \tag{5}$$

with, for example (the other blocks are defined likewise)

$$H_{\mu\nu}^{(\alpha\beta)} = \left\langle \begin{pmatrix} B_\mu \\ 0 \end{pmatrix} \middle| \hat{h} \middle| \begin{pmatrix} 0 \\ B_\nu \end{pmatrix} \right\rangle \tag{6}$$

Most two-component density functional programs seem to use such a representation of spin-dependent operators through the matrix elements with two-component basis functions, but our implementation is different as we express the spin-dependent operator $\hat{h}$

$$\hat{h} = \hat{h}^{(0)} + \sigma_x \hat{h}^{(x)} + \sigma_y \hat{h}^{(y)} + \sigma_z \hat{h}^{(z)} \tag{7}$$

through *spin-free* operators $\hat{h}^{(0)}$, $\hat{h}^{(x)}$, $\hat{h}^{(y)}$ and $\hat{h}^{(z)}$ and the Pauli spin matrices. This can be done for any spin-dependent one-particle operator. In the absence of magnetic fields, the Hamiltonian $\hat{h}$ is invariant w.r.t. time reversal, that is

$$\hat{h} = \hat{T}\hat{h}\hat{T}^{-1} \tag{8}$$

$$\hat{T} = -\mathrm{i}\,\sigma_y \hat{C} \tag{9}$$

($\hat{C}$ is the complex conjugation operator), and a little algebra shows then that

$$\hat{h}^{(0)} = \hat{C}\hat{h}^{(0)}\hat{C} \tag{10}$$

$$\hat{h}^{(S)} = -\hat{C}\hat{h}^{(S)}\hat{C}, \quad S \in \{x, y, z\} \tag{11}$$

Internally, we represent the operator $\hat{h}$ through the matrix elements of these spin-free operators, and this gives four $N \times N$ matrices $\mathbf{H}^{(0)}$, $\mathbf{H}^{(x)}$, $\mathbf{H}^{(y)}$ and $\mathbf{H}^{(z)}$ with, for example (the other matrices are defined likewise)

$$H_{\mu\nu}^{(x)} = \left\langle B_\mu \middle| \hat{h}^{(x)} B_\nu \right\rangle \tag{12}$$

Switching to this representation has several advantages. For example, from Eqs.(10,11) follows that for real basis functions ($B_\mu = \hat{C} B_\mu$) the matrix $\mathbf{H}^{(0)}$ is real while the matrices $\mathbf{H}^{(x)}$, $\mathbf{H}^{(y)}$ and $\mathbf{H}^{(z)}$ are purely imaginary, and only their imaginary part need be stored. Compared to the full matrix $\mathbf{H}$ (or its four blocks), our representation needs only half of the storage. The full complex $2N \times 2N$ matrix can easily be constructed through

$$\mathbf{H}^{(\alpha\alpha)} = \mathbf{H}^{(0)} + \mathbf{H}^{(z)}, \quad \mathbf{H}^{(\alpha\beta)} = \mathbf{H}^{(x)} - \mathrm{i}\mathbf{H}^{(y)}$$

$$\tag{13}$$

$$\mathbf{H}^{(\beta\beta)} = \mathbf{H}^{(0)} - \mathbf{H}^{(z)}, \quad \mathbf{H}^{(\beta\alpha)} = \mathbf{H}^{(x)} + \mathrm{i}\mathbf{H}^{(y)}$$

The only occasion where this is actually done in our program is for the matrix representation of the Fock (Kohn-Sham) operator before it is transformed to the molecular orbital basis as part of the diagonalization, because this enables us to use BLAS routines for the matrix multiplications that are part of this transformation (see Sec. 3).

The one-electron part of the energy expectation value of the Slater determinant Ψ is

$$E_{1e} = \sum_{i=1}^{n} < \psi_i | \hat{h} \psi_i >$$

$$= \sum_{\mu,\nu=1}^{N} \left\{ D_{\mu\nu}^{(0)} H_{\mu\nu}^{(0)} + D_{\mu\nu}^{(x)} H_{\mu\nu}^{(x)} + D_{\mu\nu}^{(y)} H_{\mu\nu}^{(y)} + D_{\mu\nu}^{(z)} H_{\mu\nu}^{(z)} \right\} \tag{14}$$

This defines the density matrices $\mathbf{D}^{(0)}$, $\mathbf{D}^{(x)}$, $\mathbf{D}^{(y)}$ and $\mathbf{D}^{(z)}$ which can be computed from the molecular orbital coefficients as

$$D_{\mu\nu}^{(0)} = \sum_{i=1}^{n} \left\{ \left(C_{\mu i}^{(\alpha)} \right)^{\star} C_{\nu i}^{(\alpha)} + \left(C_{\mu i}^{(\beta)} \right)^{\star} C_{\nu i}^{(\beta)} \right\}$$

$$D_{\mu\nu}^{(x)} = \sum_{i=1}^{n} \left\{ \left(C_{\mu i}^{(\alpha)} \right)^{\star} C_{\nu i}^{(\beta)} + \left(C_{\mu i}^{(\beta)} \right)^{\star} C_{\nu i}^{(\alpha)} \right\}$$

$$D_{\mu\nu}^{(y)} = -\mathrm{i} \sum_{i=1}^{n} \left\{ \left(C_{\mu i}^{(\alpha)} \right)^{\star} C_{\nu i}^{(\beta)} - \left(C_{\mu i}^{(\beta)} \right)^{\star} C_{\nu i}^{(\alpha)} \right\} \tag{15}$$

$$D_{\mu\nu}^{(z)} = \sum_{i=1}^{n} \left\{ \left(C_{\mu i}^{(\alpha)} \right)^{\star} C_{\nu i}^{(\alpha)} - \left(C_{\mu i}^{(\beta)} \right)^{\star} C_{\nu i}^{(\beta)} \right\}$$

To compute E_{1e}, only the real part of $\mathbf{D}^{(0)}$ and the imaginary parts of $\mathbf{D}^{(x)}$, $\mathbf{D}^{(y)}$ and $\mathbf{D}^{(z)}$ are needed and thus requires $4N^2$ (real) floating point multiplications (not counting the hermiticity of the $\mathbf{D}$ and $\mathbf{H}$ matrices, which leads to the same savings in both representations). The computational effort to contract the (complex) $2N \times 2N$ matrix $\mathbf{H}$ with the corresponding (complex) density matrix is at least twice as high.

So far we have not imposed any constraints on the molecular orbitals ψ_i except being normalized and orthogonal. This is known as as the *Kramers unrestricted* procedure, it corresponds to spin unrestricted Kohn-Sham and Hartree-Fock formalisms. Since spin restricted methods are rarely used in nonrelativistic density functional theory, so we did not implement the two-component *Kramers restricted* case either. We do however obtain a reduction both in storage and CPU time for the *closed shell* case, where all the orbitals ψ_i form Kramers pairs (n is necessarily even in this case). Two orbitals ψ_i and ψ_j form a Kramers pair if (except for a phase factor) they are related through

$$\psi_j = \begin{pmatrix} \phi_j^{(\alpha)} \\ \phi_j^{(\beta)} \end{pmatrix} = \begin{pmatrix} -\left(\phi_i^{(\beta)}\right)^{\star} \\ \left(\phi_i^{(\alpha)}\right)^{\star} \end{pmatrix} = -\mathrm{i}\,\sigma_y \hat{C} \psi_i \tag{16}$$

Because the basis functions are real, one can verify that in the *closed shell* case, $\mathbf{D}^{(0)}$ is real while $\mathbf{D}^{(x)}$, $\mathbf{D}^{(y)}$ and $\mathbf{D}^{(z)}$ are purely imaginary. This does not only halve the storage needed for the density matrices but also leads to considerable computational savings when calculating the contributions from the electron interaction to the Kohn-Sham (Fock) matrix, and implies that the spin density vanishes everywhere (see below).

The electron interaction part of the energy expectation value is

$$E_{2e} = \frac{1}{2} \sum_{i,j=1}^{n} \left\{ (\psi_i \psi_i | \psi_j \psi_j) - a_X (\psi_i \psi_j | \psi_j \psi_i) \right\}$$

$$+ \int F_{xc} \left(\rho(\vec{r}), s(\vec{r}) \right) \mathrm{d}\vec{r} \tag{17}$$

In the Hartree-Fock case, $a_X = 1$ and F_{xc} vanishes, while for pure density functionals, $a_X = 0$. For the so-called hybrid (or exact exchange) density functionals first suggested by Becke [21,22] F_{xc} is non-vanishing and a_X assumes a non-zero value (frequently around 0.2). As written here, the function $F_{xc}(\vec{r})$ depends locally on the density $\rho(\vec{r})$ and the spin density $s(\vec{r})$ (local density approximation). Modern 'gradient-corrected' functionals additionally depend on the derivatives $\vec{\nabla}\rho \cdot \vec{\nabla}\rho$, $\vec{\nabla}\rho \cdot \vec{\nabla} s$ and $\vec{\nabla} s \cdot \vec{\nabla} s$. Although this case has been implemented as well (some details can be found in Ref. [23]), it will not be discussed here since it is a straightforward albeit tedious extension well known from the nonrelativistic case.

The first contribution to E_{2e} involves two-electron integrals with two-component orbitals in Mulliken notation, which can be expressed in conventional two-electron integrals (involving only scalar orbitals) for arbitrary spinors ψ_p

$$(\psi_p\psi_q|\psi_r\psi_s) = (\phi_p^{(\alpha)}\phi_q^{(\alpha)}|\phi_r^{(\alpha)}\phi_s^{(\alpha)}) + (\phi_p^{(\alpha)}\phi_q^{(\alpha)}|\phi_r^{(\beta)}\phi_s^{(\beta)})$$

$$+ (\phi_p^{(\beta)}\phi_q^{(\beta)}|\phi_r^{(\alpha)}\phi_s^{(\alpha)}) + (\phi_p^{(\beta)}\phi_q^{(\beta)}|\phi_r^{(\beta)}\phi_s^{(\beta)}) \tag{18}$$

To facilitate the notation we use the conventional definition of the Coulomb and exchange operators $\hat{J}$ and $\hat{K}$ which are defined through their matrix elements

$$<\psi_p|\hat{J}\psi_q> = \sum_{j=1}^{n}(\psi_p\psi_q|\psi_j\psi_j)$$

$$<\psi_p|\hat{K}\psi_q> = \sum_{j=1}^{n}(\psi_p\psi_j|\psi_j\psi_q) \tag{19}$$

In the matrix representation in terms of our real basis functions, $\mathbf{J}^{(0)}$ is a real matrix and $\mathbf{J}^{(x)}$, $\mathbf{J}^{(y)}$, $\mathbf{J}^{(z)}$ vanish (because $\hat{J}$ is a spin-free operator). The two-electron energy can be re-expressed as

$$E_{2e} = \frac{1}{2}\sum_{\mu,\nu=1}^{N} D_{\mu\nu}^{(0)} J_{\mu\nu}^{(0)}$$

$$- \frac{a_X}{4}\sum_{\mu,\nu=1}^{N}\left\{D_{\mu\nu}^{(0)}K_{\mu\nu}^{(0)} + D_{\mu\nu}^{(x)}K_{\mu\nu}^{(x)} + D_{\mu\nu}^{(y)}K_{\mu\nu}^{(y)} + D_{\mu\nu}^{(z)}K_{\mu\nu}^{(z)}\right\} \tag{20}$$

$$+ \int F_{xc}\left(\rho(\vec{r}), s(\vec{r})\right) \mathbf{d}\vec{r}$$

The $\mathbf{J}$ and $\mathbf{K}$ matrices can be calculated from the conventional two-electron integrals using standard techniques

$$J_{\mu\nu}^{(0)} = \sum_{\rho,\sigma=1}^{N} D_{\rho\sigma}^{(0)}(B_\mu B_\nu|B_\rho B_\sigma)$$

$$K_{\mu\nu}^{(S)} = \sum_{\rho,\sigma=1}^{N} D_{\rho\sigma}^{(S)}(B_\mu B_\sigma|B_\rho B_\nu), \quad S \in \{0, x, y, z\} \tag{21}$$

Note that only the real part of $\mathbf{D}^{(0)}$ is needed to construct $\mathbf{J}^{(0)}$, such that the algorithm from a nonrelativistic program can be used without any change. The exchange operator is spin-dependent even for *closed shell* systems, but in this special case $\mathbf{K}^{(0)}$ is real and $\mathbf{K}^{(x)}$, $\mathbf{K}^{(y)}$, $\mathbf{K}^{(z)}$ are purely imaginary. This follows from the properties of the density matrices and the fact that the two-electron integrals $(B_\mu\, B_\sigma \mid B_\rho\, B_\nu)$ are real. In fact we store the real and imaginary parts of the density matrices separately and thus also separately construct the real and imaginary parts of the $\mathbf{K}$ matrices using well-tested code from our nonrelativistic program. In addition, half of the work can just be skipped in the *closed shell* case where the imaginary part of $\mathbf{K}^{(0)}$ and the real parts of $\mathbf{K}^{(x)}$, $\mathbf{K}^{(y)}$ and $\mathbf{K}^{(z)}$ vanish and need not be computed. Comparing the computational effort of a scalar relativistic and a two-component program, there is no difference in the calculation of the matrix elements of $\hat{J}$, but for the $\mathbf{K}$ matrices the *processing* of the two-electron integrals is four times more expensive (the *calculation* of the two-electron integrals is the same of course). The exchange-correlation energy is evaluated using numerical quadrature as in the nonrelativistic case. At each grid point of the integration grid, one needs to evaluate the density and the spin density. The density is given by

$$\rho(\vec{r}) = \sum_{i=1}^{n} \psi_i^\dagger(\vec{r})\psi_i(\vec{r}) = \sum_{\mu,\nu=1}^{N} D_{\mu\nu}^{(0)} B_\mu(\vec{r}) B_\nu(\vec{r}) \tag{22}$$

Only the real part of the density matrix $\mathbf{D}^{(0)}$ contributes, such that there is no difference to the nonrelativistic implementation. In a quasirelativistic procedure is however not clear *a priori* how to define the spin density. This has been investigated in some detail in Ref. [24]. Basically, one defines a (spin) magnetization vector $\vec{m} = (m_x, m_y, m_z)$ with

$$m_x(\vec{r}) = \sum_{i=1}^{n} \psi_i^\dagger(\vec{r})\sigma_x\psi_i(\vec{r}) = \sum_{\mu,\nu=1}^{N} D_{\mu\nu}^{(x)} B_\mu(\vec{r}) B_\nu(\vec{r})$$

$$m_y(\vec{r}) = \sum_{i=1}^{n} \psi_i^\dagger(\vec{r})\sigma_y\psi_i(\vec{r}) = \sum_{\mu,\nu=1}^{N} D_{\mu\nu}^{(y)} B_\mu(\vec{r}) B_\nu(\vec{r}) \tag{23}$$

$$m_z(\vec{r}) = \sum_{i=1}^{n} \psi_i^\dagger(\vec{r})\sigma_z\psi_i(\vec{r}) = \sum_{\mu,\nu=1}^{N} D_{\mu\nu}^{(z)} B_\mu(\vec{r}) B_\nu(\vec{r})$$

Note that again only the real parts of the density matrices contribute. These are zero in the *closed shell* case where of course $\vec{m} = 0$ everywhere (and need not be computed). There are two ways to define the spin density in terms of $\vec{m}$, and both have been implemented in our program. The older one is the *collinear approach*, where one chooses a unit vector $\vec{e} = (e_x, e_y, e_z)$ (frequently called the spin alignment direction or the spin quantization axis) pointing in an arbitrary but fixed direction, and defines $s(\vec{r}) = \vec{e} \cdot \vec{m}(\vec{r})$. It has been pointed out [24] that the collinear approach together with spin-orbit coupling lets the total energy of a molecule depend on its orientation which is not desirable in most cases (an

exception is the calculation of magnetic anisotropy energies, see below). An energy expression that is rotationally invariant results from the *non-collinear approach* where one defines $s(\vec{r}) = |\vec{m}(\vec{r})|$. The non-collinear approach requires a larger computational effort since one has to calculate the three quantities m_x, m_y, m_z at each grid point before evaluating the spin density there, while in the collinear approach one first constructs a single effective spin density matrix $\mathbf{D}^{(e)}$ and evaluates the spin density at each point as

$$\mathbf{D}^{(e)} = e_x \mathbf{D}^{(x)} + e_y \mathbf{D}^{(y)} + e_z \mathbf{D}^{(z)}$$

$$s(\vec{r}) = \sum_{\mu,\nu=1}^{N} D_{\mu\nu}^{(e)} B_\mu(\vec{r}) B_\nu(\vec{r}) \tag{24}$$

To optimize the orbitals, matrix elements of the Fock (or Kohn-Sham) operator

$$\hat{F} = \hat{h} + \hat{J} - a_x \hat{K} + V_{xc} \tag{25}$$

are needed, all of them have been discussed except for the exchange-correlation potential V_{xc}. For real basis functions all the matrix representations $\mathbf{V}_{xc}^{(0)}$, $\mathbf{V}_{xc}^{(x)}$, $\mathbf{V}_{xc}^{(y)}$ and $\mathbf{V}_{xc}^{(z)}$ are real, and $\mathbf{V}_{xc}^{(0)}$ is calculated as in the nonrelativistic case

$$\left(V_{xc}^{(0)}\right)_{\mu\nu} = \int B_\mu B_\nu \frac{\delta F_{xc}}{\delta\rho}\,\mathrm{d}\vec{r} \tag{26}$$

This means that in the closed shell case, where the spin density vanishes and thus $\mathbf{V}_{xc}^{(x)} = \mathbf{V}_{xc}^{(y)} = \mathbf{V}_{xc}^{(z)} = 0$, the exchange-correlation part of a two-component density functional calculation needs nothing beyond that already available from the nonrelativistic implementation. In the collinear approach, one calculates a single effective spin-dependent matrix $\mathbf{V}_{xc}^{(e)}$

$$\left(V_{xc}^{(e)}\right)_{\mu\nu} = \int B_\mu B_\nu \frac{\delta F_{xc}}{\delta s}\,\mathrm{d}\vec{r} \tag{27}$$

and constructs the matrices $V_{xc}^{(x,y,z)}$ easily through

$$\mathbf{V}_{xc}^{(x)} = e_x \mathbf{V}_{xc}^{(e)}, \quad \mathbf{V}_{xc}^{(y)} = e_y \mathbf{V}_{xc}^{(e)}, \quad \mathbf{V}_{xc}^{(z)} = e_z \mathbf{V}_{xc}^{(e)} \tag{28}$$

In contrast, one has to construct three independent matrices in the non-collinear approach (all quantities in the integrands depend on $\vec{r}$)

$$\left(V_{xc}^{(x)}\right)_{\mu\nu} = \int B_\mu B_\nu \frac{m_x}{s} \frac{\delta F_{xc}}{\delta s}\,\mathrm{d}\vec{r}$$

$$\left(V_{xc}^{(y)}\right)_{\mu\nu} = \int B_\mu B_\nu \frac{m_y}{s} \frac{\delta F_{xc}}{\delta s}\,\mathrm{d}\vec{r} \tag{29}$$

$$\left(V_{xc}^{(z)}\right)_{\mu\nu} = \int B_\mu B_\nu \frac{m_z}{s} \frac{\delta F_{xc}}{\delta s}\,\mathrm{d}\vec{r}$$

Thus, for *closed shell* systems and also *open shell* systems with the collinear approach, the computational effort for the two-component exchange-correlation part is the same as for the nonrelativistic case (actually the same code is used), while the effort is doubled for the *open shell* case in the non-collinear approximation.

Geometry gradients for this formalism have been implemented [23] using well-established techniques, provided that the geometrical derivatives of the matrix elements of the quasirelativistic Hamiltonian $\hat{h}$ are available (see Sec. 4). There is little difference in CPU time betweeen the nonrelativistic and the two-component gradient since both are dominated by the calculation of the derivative two-electron integrals.

Early implementations of the two-component density functional method were restricted the collinear approach with a single 'hard-wired' spin alignment direction $\vec{e} = (0,0,1)$. This has largely been abandoned because of the loss of rotational invariance caused by singling out a spin alignment direction [24]. For a special application, namely the calculation of magnetic anisotropy energies (or zero field splittings) the collinear approach is however the method of choice [25–27]. Because of the spin-orbit interaction (together with relativistic corrections to the electron interaction), the ground state energy of a (laboratory-fixed) molecule in a strong homogeneous external magnetic field depends on the relative orientation of the molecule and the magnetic field. This dependence is called the magnetic anisotropy energy and is closely related to zero field splitting. Note that the relation between these two quantities has not always been fully understood, such that too small zero field splitting parameters have been extracted from magnetic anisotropy calculations [27]. To calculate magnetic anisotropy energies with density functional methods, one could expose the molecule an external magnetic field strong enough to align the spins but that does not mix Zeeman levels of different spin states (that is, increase the overall spin polarization). For this special purpose it is better to use the collinear definition of the spin density, because this will create an effective magnetic field that aligns the spins where there is spin density, but vanishes elsewhere. With this application in mind we have implemented the collinear approach in its full generality, that is, for any quantization axis $\vec{e}$ given by the user in the program input. Starting from scalar relativistic orbitals (where $\vec{m}(\vec{r})$ is parallel to the z axis everywhere) we first rotate the spins such that $\vec{m}$ is parallel to $\vec{e}$ everywhere, and iterate until self-consistency using the collinear approach. This is repeated for several different directions $\vec{e}$ and a magnetic anisotropy energy profile thus generated (for an application to the extensively studied molecular magnet $Mn_{12}O_{12}$ acetate, a system with nearly 150 atoms, see Ref. [27]).

3. Efficiency and Parallelization

In a typical calculation on a molecular system of about 100 atoms, the calculation of the $\mathbf{J}$, $\mathbf{K}$ (for $a_x \neq 0$) and $\mathbf{V}_{xc}$ (for $F_{xc} \neq 0$) matrices requires the largest part of the CPU time. While the calculation of $\mathbf{J}$ is the same for a nonrelativistic (or scalar-relativistic) and a two-component calculation with the same basis set (actually the same code is used), calculating $\mathbf{V}_{xc}$ in the two-component non-collinear approach is twice as expensive, and *processing* the two-electron integrals to

construct **K** even requires four times more floating point operations compared to the nonrelativistic case. Since the effort to *calculate* the two-electron integrals is the same in either case, we estimate that for Hartree-Fock and exact exchange containing density functionals, the effort associated with two-electron integrals is twice as large for the two-component calculations. After having properly implemented Pulay's "FDS-SDF" convergence accelerator [28] for the two-component case, the number of SCF iterations is similar for scalar-relativistic and two-component calculations on the same molecule, such that a two-component calculation is about twice as expensive as a scalar-relativistic calculation. The construction of the Fock matrix (calculation/processing of the two-electron integrals, numerical integration) can be parallelized using the same techniques as in the nonrelativistic case and need not be discussed here, but it is important to realize that the remaining, non-parallelized matrix algebra steps (the transformation of the Fock matrix to the molecular orbital basis, the diagonalization of the resulting matrix, the MO orthogonalization every few iterations, and the Pulay procedure) have a higher relative cost in the two-component case. This stems from the fact that matrix dimensions are twice as large (this gives a factor of eight because the effort for matrix multiplications and diagonalizations scales cubically with the dimension) and complex (this gives another factor of four). This analysis is supported by computer experiments [16]. To obtain good parallelization efficiency up to 32 parallel CPUs, all matrix algebra is done by BLAS and LAPACK routines (notably, subroutines zgemm for matrix multiplication, zheevd for matrix diagonalization, and zpotrf as well as ztrsm for MO orthogonalization via Cholesky decomposition). As an additional advantage, multithreaded BLAS and LAPACK libraries are available that give a certain degree of automatic parallelization of these matrix routines on modern multicore CPUs. This together brings down the wall-clock time for the matrix steps well below that for the construction of the Fock matrix even in a parallel calculation. The overall efficiency of the two-component program is thus such that almost every scalar-relativistic calculation that can be done is also possible using the correspondig spin-dependent (two-component) quasirelativistic Hamiltonian.

In Table 1, CPU times (in seconds, single 2.8 GHz Xeon CPU core) for matrix operations (building the density matrices, similarity transformations, diagonlizations), the calculation and processinig of two-electron integrals, and the numerical quadrature are reported for a single SCF iteration on the *open shell* gold cluster Au_{21} and the *closed shell* system obtained by adsorbing a Tl atom onto it. ECPs were used in these calculations, and a $7s7p7d1f$ primitive basis set, contracted to $5s5p4d1f$ was used for Au, while $7s8p7d1f$ contracted to $5s6p4d1f$ was used for Tl. For Au_{21} there were 987 contracted scalar basis functions and our (fairly accurate) integration grid had ~ 457000 grid points with nonzero weight (1037 basis functions and ~ 476000 grid points for $Au_{21}Tl$). The measured CPU times are consistend with the analysis given above. Point-group symmetry has not been used in any of these calculations because it has not been implemented for the two-component case. The proper implementation of double

Table 1. CPU time for a single SCF iteration for scalar-relativistic ("sc") and two-component ("2c") ECP calculation for $Au_{21}Tl$ (*closed shell*) and Au_{21} (*open shell*). Results are given for a gradient-corrected (BP) and an exact-exchange containing (B3LYP) exchange-correlation functional. See text for computational details.

Molecule			matrix operations	two-electron integrals [a]	numerical quadrature
$Au_{21}Tl$	BP	sc	2	1594	90
		2c	45	1602	90
	B3LYP	sc	2	2273	90
		2c	44	5091	90
Au_{21}	BP	sc	3	1406	174
		2c	39	1409	406
	B3LYP	sc	3	2418	174
		2c	39	5259	405

[a] time for *both* calculating and processing the two-electron integrals

group symmetry as necessary for two-component calculations is slightly more complicated than in the scalar-relativistic or nonrelativistic case, on the other hand we expect smaller computational savings because the relativistic symmetry is usually lower. For example, there is only a single fermion irrep in the relativistic (double) point groups C_{2v}^* and D_2^*.

4. Quasirelativistic Hamiltonians

The ZORA Hamiltonian, which goes back to Ref. [29], has been thoroughly investigated (and given the name ZORA) by the Amsterdam group [30–32] and found much use in relativistic quantum chemistry since then. In our implementation, the ZORA matrix elements are evaluated through numerical quadrature, which makes the implementation of the spin-orbit parts and their geometrical derivatives quite facile. There is a fundamental problem with ZORA, namely that it is not gauge invariant. Different implementations of ZORA have introduced different methods to work around this problem, and our approach, the 'model potential' variant of ZORA [33, 34] is the only one that does *not* rely on a mapping of basis functions to nuclear centers. Systematic improvements beyond the ZORA model [35,36] have not found much use.

There is another quasirelativistic all-electron Hamiltonian of comparable popularity, namely the Douglas-Kroll-Hess approach. For a rececnt review of its concepts see Ref. [37]. For more than a decade, it has only been used at its second order, extensions beyond [38,39] have revealed that the Douglas-Kroll Hamiltonian is not uniquely defined beyond the fourth order. This was not understood and quite baffling until it was clearly analyzed by the present author [40] on the occasion of formulating sixth-order Douglas-Kroll for the first time. Nu-

merical experiments have shown that for one-electron systems, positive-energy Dirac eigenvalues can be reproduced by Douglas-Kroll to any desired accuracy if one extends the order of the Douglas-Kroll Hamiltonian far enough [41,42]. However, getting numerically exact results for one-electron systems is not sufficient: it is also necessary to include the electron interaction contribution to the effective potential when constructing the Douglas-Kroll Hamiltonian since otherwise large errors for spin-orbit splittings [12] or magnetic anisotropies [27] arise. Second, for high accuracy one has to compensate that the physical (or "true") electron density cannot directly be calculated from the two-component orbitals (the so-called *picture change effect*). A treatment of the electron interaction including full account of the picture change effect would be even more expensive than performing a fully relativistic four-component calculation in the first place, therefore higher-order Douglas-Kroll Hamiltonians only make sense if there is an efficient but still accurate approximation to the electron interaction part. Stimulated by the success of the 'model potential' approximation in the ZORA framework, we have suggested an approximation along the same lines for Douglas-Kroll [43]. It relies on the observation that the largest differences between the "true" electron density and those calculated from the two-component orbitals occur in the inner cores of the atoms where they are not very sensitive to the chemical environment. Information from atomic calculations (performed once and forever) can thus be used to correct the density obtained from the two-component orbitals.

Most scalar relativistic calculations performed today probably use effective core potentials (ECPs). For a recent review focusing on the type of ECPs mostly used in our applications, see Ref. [44]. It is straightforward to include spin-orbit terms in such ECPs, and the techniques to evaluate the molecular integrals that arise are well known [45,46]. We have implemented these integrals in our program and could improve the computational efficiency quite a bit [47]. In gradient calculations geometrical derivatives of the matrix elements of the quasirelativistic Hamiltonian are needed. We extended the techniques known from the scalar-relativistic case to implement geometrical derivatives of the spin-dependent parts of the ZORA and ECP integrals [23]. These become more complicated for Douglas-Kroll, as reported by Nasluzov and Rösch [48], and will also be computationally expensive for large molecules. For ZORA a so-called *strictly atomic* approximation has been suggested [49] where relativistic corrections are applied only to one-center atomic matrix elements. Within such an approximation, that also been suggested in the framework of Douglas-Kroll [50], relativistic correction to the geometrical derivatives of the one-particle Hamiltonian matrix elements vanish and need not be calculated.

Our experience [11,23,47,51] shows that very similar molecular structures and vibrational frequencies (and to a large extent also binding energies) are obtained from fully relativistic four-component and quasirelativistic ZORA or Douglas-Kroll calculations. In the latter case, it is hardly necessary to go beyond the fourth order for these properties. Note that our comparison is limited to

diatomic molecules since we did not implement the geometrical derivatives of the Douglas-Kroll matrix elements, as this seems unnecessary in view of the above observation. A statement of similar generality cannot be made for ECPs since some variations between ECPs from different sources have been found. However, for systems with many heavy atoms *any* type of all-electron calculation (let it be nonrelativistic, scalar-relativistic or two-component) is rather expensive and ECPs furnish a quite attractive alternative there.

5. Conclusions

If properly implemented, a quasirelativistic two-component density functional or Hartree-Fock program exhibits the same efficiency we are used to in nonrelativistic calculations, and our strategy to achieve this has been presented in this article. Issues specific to the two-component formalism are how to define the spin density (collinear vs. non-collinear approach) and the higher relative weight of the linear algebra steps in the SCF procedure which needs to be considered when parallelizing the code. Through the availabilty of forces (geometry gradients), automatic geometry optimizations can be carried out which is a prerequisite for obtaining molecular structures and binding energies for polyatomic compounds. We must however admit that spin-orbit effects on molecular structures are rather small for most chemical compounds. The magnetic anisotropy energy on the other hand is a property which not only depends strongly on spin-orbit coupling, but is a genuine relativistic effect as it would vanish in a nonrelativistic or scalar-relativistic world. Therefore, a two-component description is really needed if one is interested in magnetic anisotropy energies of molecules with heavy atoms.

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