

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/11359928>

# Four-Component Relativistic Kohn-Sham Theory

ARTICLE *in* JOURNAL OF COMPUTATIONAL CHEMISTRY · JUNE 2002

Impact Factor: 3.59 · DOI: 10.1002/jcc.10066 · Source: PubMed

---

CITATIONS

73

---

READS

60

2 AUTHORS, INCLUDING:



Trygve Ulf Helgaker

University of Oslo

361 PUBLICATIONS 17,565 CITATIONS

SEE PROFILE

# Four-Component Relativistic Kohn–Sham Theory

TROND SAUE,<sup>1</sup> TRYGVE HELGAKER<sup>2</sup>

<sup>1</sup>UMR 7551 CNRS/Université Louis Pasteur, Laboratoire de Chimie Quantique et Modélisation Moléculaire, 4 rue Blaise Pascal, F-67000 Strasbourg, France

<sup>2</sup>Department of Chemistry, University of Oslo, P.O. Box 1033 Blindern, N-0315 Oslo, Norway

Received 20 November 2001; Accepted 14 December 2001

DOI 10.1002/jcc.10066

**Abstract:** A four-component relativistic implementation of Kohn–Sham theory for molecular systems is presented. The implementation is based on a nonredundant exponential parametrization of the Kohn–Sham energy, well suited to studies of molecular static and dynamic properties as well as of total electronic energies. Calculations are presented of the bond lengths and the harmonic and anharmonic vibrational frequencies of Au<sub>2</sub>, Hg<sub>2</sub><sup>2+</sup>, HgAu<sup>+</sup>, HgPt, and AuH. All calculations are based on the full four-component Dirac–Coulomb Hamiltonian, employing nonrelativistic local, gradient-corrected, and hybrid density functionals. The relevance of the Coulomb and Breit operators for the construction of relativistic functionals is discussed; it is argued that, at the relativistic level of density-functional theory and in the absence of a vector potential, the neglect of current functionals follows from the neglect of the Breit operator.

© 2002 Wiley Periodicals, Inc. J Comput Chem 23: 814–823, 2002

**Key words:** Kohn–Sham theory; four-component relativistic implementation

## Introduction

The universal acceptance of the periodic table towards the end of the 19th century was in large part due to Mendeleev's successful prediction<sup>1</sup> of the properties of gallium, scandium, and germanium—elements unknown in 1871. However, if the vacant slots had been located in the lower part of the periodic table, the predictions of Mendeleev are likely to have been less convincing. The prime origin of the deviation from the periodic behavior for the heavier elements is relativity.<sup>2,3</sup> Indeed, over the past 30 years, the inclusion of the effects of relativity has become an essential ingredient in theoretical studies of heavy-element chemistry.

However, in the high-*Z* regime, the effects of electron correlation can be just as important as those of relativity, making it important to develop efficient methods for the simultaneous treatment of correlation and relativity. The density-functional theory (DFT) has shown itself very capable of treating electron correlation at a reasonable computational cost.<sup>4</sup> Relativistic DFT has been formulated within the framework of quantum electrodynamics, where the renormalization procedure provides a minimum principle that has made possible the relativistic extension<sup>5</sup> of the Hohenberg–Kohn theorem.<sup>6</sup> Subsequently, relativistic versions of the Kohn–Sham equations have been developed independently by Rajagopal<sup>7</sup> and by MacDonald and Vosko.<sup>8</sup> Recent reviews of relativistic DFT have been given by Engel and Dreizler<sup>9</sup> and by Engel et al.<sup>10</sup>

The combination of DFT and relativistic treatments has now found its way into many quantum-chemistry software packages,

mostly within the framework of one- and two-component schemes,<sup>11</sup> although some four-component implementations have also been reported (see refs. <sup>12, 13</sup>, and <sup>14</sup>, and references therein). In this article, we report the implementation of four-component relativistic DFT based on nonrelativistic functionals in the molecular code DIRAC.<sup>15</sup> Among the current four-component relativistic molecular programs, DIRAC has the greatest functionality. It is hoped that the inclusion of DFT in DIRAC can facilitate the extension of the four-component relativistic Kohn–Sham method to properties beyond spectroscopic constants, such as excitation energies and various electric and magnetic properties.

## Theory

The theory part consists of four sections. We first discuss the structure of the molecular relativistic Hamiltonian in the next subsection, emphasizing those aspects that are relevant for DFT, in particular the significance of the Coulomb and Gaunt operators. Next, we consider the Kohn–Sham energy and its parameterization in terms of a set of nonredundant variational parameters. A general technique for expanding the Kohn–Sham energy in the variational parameters is then presented and applied to first order. Finally, we discuss some aspects related to the optimization of the Kohn–Sham energy.

**Correspondence to:** T. Helgaker; e-mail: trygve.helgaker@kjemi.uio.no

### The Dirac–Coulomb Hamiltonian

The DFT calculations reported in this article are based on the Dirac–Coulomb Hamiltonian

$$\hat{H}_{\text{DC}} = \sum_i \hat{h}_{\text{D},i} + \sum_i \hat{V}_i^{\text{ext}} + \frac{1}{2} \sum_{i \neq j} \hat{g}_{ij}^{\text{Coul}} + V_{\text{NN}} \quad (1)$$

for a system of  $N$  electrons in the field of  $n$  fixed nuclei. In this expression,  $\hat{h}_{\text{D},i}$  is the free-particle Dirac operator of electron  $i$  (atomic units)

$$\hat{h}_{\text{D},i} = \begin{bmatrix} \mathbf{0}_2 & c(\boldsymbol{\sigma}_i \cdot \mathbf{p}_i) \\ c(\boldsymbol{\sigma}_i \cdot \mathbf{p}_i) & -2c^2 \mathbf{I}_2 \end{bmatrix}, \quad (2)$$

and  $\hat{V}_i^{\text{ext}}$  is the external potential, which, in the absence of an external electromagnetic field, takes the form

$$\hat{V}_i^{\text{ext}} = - \sum_K \frac{Z_K}{r_{iK}} \mathbf{I}_4. \quad (3)$$

In eq. (2),  $c$  is the velocity of light in vacuum,  $m$  the mass of the electron,  $\boldsymbol{\sigma}_i$  the Pauli spin matrices of electron  $i$ , and  $\mathbf{p}_i$  its linear momentum; in eq. (3),  $Z_K$  is the charge of nucleus  $K$  and  $r_{iK}$  its distance from electron  $i$ . In passing, we note that, in the Born–Oppenheimer approximation, there is a preferred reference frame for the electrons—namely, the frame in which the nuclei are at rest. This is still acceptable within the framework of Lorentz invariant theory, but in reality there is no frame in which all nuclei are at rest.

The two-electron interaction in the Hamiltonian eq. (1) is given by the Coulomb term

$$\hat{g}_{ij}^{\text{Coul}} = \frac{\mathbf{I}_4 \cdot \mathbf{I}_4}{r_{ij}}, \quad (4)$$

which is Lorentz variant as it describes an instantaneous interaction. It is best considered the zeroth-order term of a perturbation expansion of the fully relativistic electron–electron interaction. We note that, even though the Coulomb term appears to have the same mathematical form as in the nonrelativistic domain, its physical content is rather different (e.g., it also contains the spin–own-orbit interaction), as emphasized by expressing the operator in terms of the  $4 \times 4$  identity matrices  $\mathbf{I}_4$ .

The description of the electron–electron interaction can be improved upon by the introduction of the Breit term

$$\hat{g}_{ij}^{\text{Breit}} = \hat{g}_{ij}^{\text{Gaunt}} + \hat{g}_{ij}^{\text{gauge}}, \quad (5)$$

which has here been split into the Gaunt term and what has been denoted a gauge term:

$$\hat{g}_{ij}^{\text{Gaunt}} = - \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}}; \quad \hat{g}_{ij}^{\text{gauge}} = - \frac{(\boldsymbol{\alpha}_i \cdot \nabla_i)(\boldsymbol{\alpha}_j \cdot \nabla_j)r_{ij}}{2}. \quad (6)$$

From a pragmatic point of view, we may introduce only the Gaunt term, which carries the full spin–other-orbit interaction,<sup>16</sup> but requires no new two-electron integrals. In this article, however, we do not go beyond the Coulomb approximation, as various studies have shown that the Breit term has a negligible effect on molecular spectroscopic constants.<sup>17,18</sup> Nevertheless, to get the correct atomic splittings, the Gaunt or full Breit term should be included, in particular for light elements.

Our choice of Dirac–Coulomb Hamiltonian eq. (1) has an important consequence for the choice of density functionals. To see this, let us examine in some detail the introduction of external fields and the treatment of two-electron interactions. Consider first the introduction of external fields in the free-particle Dirac operator by the principle of minimal electromagnetic coupling:<sup>19</sup>

$$p \rightarrow p - q\mathbf{A}; \quad E \rightarrow E - q\phi. \quad (7)$$

These substitutions involve the specification of the charge  $q$  interacting with the external fields; we here set  $q = -1$ , thus restricting our attention to electrons rather than positrons. Consider next the expectation value of the resulting Hamiltonian with respect to the electronic wave function  $\Psi$ , in particular, the part of the expectation value that contains the external potentials:

$$E^{\text{ext}} = -\langle \Psi | \phi - c(\boldsymbol{\alpha} \cdot \mathbf{A}) | \Psi \rangle = - \int \rho(\mathbf{r})\phi(\mathbf{r})d\mathbf{r} + \int \mathbf{j}(\mathbf{r}) \cdot \mathbf{A}(\mathbf{r})d\mathbf{r}. \quad (8)$$

The first term is straightforwardly interpreted as the energy of interaction of the scalar potential  $\phi$  with the central quantity of DFT—namely, the electron density  $\rho$ :

$$\rho(\mathbf{r}_1) = N \int \Psi^\dagger(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (9)$$

Likewise, the second term is the interaction of the vector potential  $\mathbf{A}$  with the current electron density:

$$\mathbf{j}(\mathbf{r}_1) = N \int \Psi^\dagger(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \times c\boldsymbol{\alpha}_1 \Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (10)$$

Note that, because of the spinor structure of the one-particle basis from which the full many-electron wave function is constructed, the integration does not involve spin coordinates. Also observe that, just like the charge density of electromagnetism is obtained from the electron density eq. (9) by multiplication by the charge of the electron  $-e$ , the current density is obtained from the current electron density eq. (10) by multiplication by  $-e$ .

Next, turning our attention to the two-electron interaction, the energy contribution from the Coulomb term

$$E^{\text{Coul}} = \frac{1}{2} \sum_{ij} \left\langle \Psi \left| \frac{\mathbf{I}_i \cdot \mathbf{I}_j}{r_{ij}} \right| \Psi \right\rangle = \frac{1}{2} \int \frac{\rho_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2 \quad (11)$$

can be expressed in terms of the two-electron density:<sup>20</sup>

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \Psi^\dagger(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \\ \times \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (12)$$

The two-electron density can be formally rewritten as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1)\rho(\mathbf{r}_2) + \rho(\mathbf{r}_1)h^{\text{xc}}(\mathbf{r}_2; \mathbf{r}_1), \quad (13)$$

thereby introducing the exchange–correlation hole, which leads to the well-known separation of the Coulomb interaction into the Hartree term  $J[\rho]$  and a nonclassical term containing the effects of exchange and correlation, in addition to self-interaction corrections. Whereas the Coulomb term eq. (11) represents charge–charge interaction, the corresponding Gaunt term describes current–current interaction

$$E^{\text{Gaunt}} = -\frac{1}{2} \sum_{ij} \left\langle \Psi \left| \frac{\boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j}{r_{ij}} \right| \Psi \right\rangle = -\frac{1}{2c^2} \int \frac{j_2(\mathbf{r}_1, \mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2, \quad (14)$$

where we have introduced what may be termed the two-electron current density:

$$j_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \int \Psi^\dagger(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) \\ \times c\boldsymbol{\alpha}_1 \cdot c\boldsymbol{\alpha}_2 \Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N) d\mathbf{r}_3 \dots d\mathbf{r}_N. \quad (15)$$

Note the factor of  $c^{-2}$  that appears upon the substitution of  $j_2(\mathbf{r}_1, \mathbf{r}_2)$  in eq. (14), reflecting the fact that the Gaunt term enters to a higher order than the Coulomb term in the perturbation expansion of the fully Lorentz invariant electron–electron interaction. Finally, by analogy with the two-electron density eq. (13), we may split the two-electron current density in two parts:

$$j_2(\mathbf{r}_1, \mathbf{r}_2) = \mathbf{j}(\mathbf{r}_1) \cdot \mathbf{j}(\mathbf{r}_2) + \mathbf{j}(\mathbf{r}_1) \cdot \mathbf{h}^{\text{Gaunt}}(\mathbf{r}_2; \mathbf{r}_1). \quad (16)$$

The first term is the scalar product of two one-electron current densities, and the second term involves the current-density counterpart of the exchange–correlation hole.

From the above analysis, we may draw the following conclusion: if we restrict our attention to the Dirac–Coulomb Hamiltonian and if we allow no external magnetic fields (or, more precisely, no vector potentials), then relativistic four-current DFT reduces to the regular DFT—that is, to a theory constructed on the basis of the density eq. (9) alone. There is no need to introduce the current density eq. (10) because, in this approximation, there are no contributions from the Gaunt term eq. (14) nor from the last

term in eq. (8). Moreover, this conclusion applies to open shells as well as to closed shells. Nevertheless, in view of the approximate nature of current functionals, it may be advantageous (as has already been demonstrated in the nonrelativistic domain) to introduce spin-dependent density functionals. In the relativistic domain, this can be accomplished as proposed by MacDonald and Vosko.<sup>8</sup> In the present article, we consider only closed-shell diatomics, and the spin dependence of functionals does not enter.

### Parametrization of the Kohn–Sham Energy

We write the Kohn–Sham energy as a sum of five terms

$$E[\rho] = T_s[\rho] + V^{\text{ext}}[\rho] + J[\rho] + E_{\text{xc}}[\rho] + V_{\text{NN}}, \quad (17)$$

the first four of which are functionals of the electron density  $\rho(\mathbf{r})$ . In nonrelativistic theory, the first term  $T_s[\rho]$  corresponds to the kinetic energy of a fictitious noninteracting system represented by a single Slater determinant  $|\tilde{0}\rangle$  and with the same density as the real interacting system; in relativistic theory,  $T_s[\rho]$  is the expectation value of the free-particle Dirac operator eq. (2) with respect to the fictitious noninteracting system:

$$T_s = \sum_i \langle \tilde{0} | \hat{h}_{D,i} | \tilde{0} \rangle. \quad (18)$$

The second and third terms in eq. (17) represent, respectively, the classical interaction of the electrons with the external potential (including the nuclear-attraction potential)  $V^{\text{ext}}[\rho]$  and the classical Coulomb interaction of the density with itself  $J[\rho]$  (the Hartree term):

$$V^{\text{ext}}[\rho] = \int \hat{V}^{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r}, \quad (19)$$

$$J[\rho] = \frac{1}{2} \iint \frac{\rho(\mathbf{r}_1)\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \quad (20)$$

The great unknown in eq. (17) is the exchange–correlation functional  $E_{\text{xc}}[\rho]$ , for which a number of approximations exist. This term contains all two-electron interactions except the Hartree term—that is, it contains the effects of electron exchange and electron correlation. It also corrects for the self-interaction present in the Hartree term and for the error in the evaluation of the kinetic energy. The last term in eq. (17) represents the nuclear–nuclear repulsion energy.

By analogy with closed-shell Hartree–Fock theory, we parametrize the Kohn–Sham determinant in terms of a unitary exponential orbital-rotation operator:

$$|\tilde{0}\rangle = \exp(-\hat{\kappa})|0\rangle; \quad \hat{\kappa} = \sum_{pq} \kappa_{pq} p^\dagger q. \quad (21)$$

The summations over  $p$  and  $q$  are over the full set of orthogonal orbitals, and the  $\kappa_{pq}$  are the elements of an anti-Hermitian matrix. The advantage of this parametrization is that the orbital-rotation

operator ensures orthonormality of the Kohn–Sham orbitals without the need to introduce Lagrange multipliers.

As written, eq. (21) contains redundancies in the sense that, for some nonzero choices of  $\kappa_{pq}$ , the reference state  $|\bar{0}\rangle$  is unaffected by the application of  $\exp(-\hat{\kappa})$ . These redundancies are easily avoided by restricting the summations in eq. (21) to occupied–unoccupied orbital pairs:

$$\hat{\kappa}_{\text{nonred}} = \sum_{ai} (\kappa_{ai} a^\dagger i - \kappa_{ai}^* i^\dagger a). \quad (22)$$

Here and in the following, we use the indices  $i, j, k$ , and  $l$  for occupied orbitals and the indices  $a, b, c$ , and  $d$  for virtual orbitals. The generic indices  $p, q, r$ , and  $s$  are used for general (unspecified) orbitals.

With the introduction of the orbital-rotation operator, the electron density can be written as

$$\rho(\mathbf{r}, \boldsymbol{\kappa}) = \sum_{pq} \tilde{D}_{pq}(\boldsymbol{\kappa}) \Omega_{pq}(\mathbf{r}), \quad (23)$$

where we have introduced the density matrix  $\tilde{D}_{pq}(\boldsymbol{\kappa})$  and the overlap distributions  $\Omega_{pq}(\mathbf{r})$ :

$$\tilde{D}_{pq}(\boldsymbol{\kappa}) = \langle \bar{0} | p^\dagger q | \bar{0} \rangle = \langle 0 | \exp(\hat{\kappa}) p^\dagger q \exp(-\hat{\kappa}) | 0 \rangle, \quad (24)$$

$$\Omega_{pq}(\mathbf{r}) = \phi_p^\dagger(\mathbf{r}) \phi_q(\mathbf{r}). \quad (25)$$

In the absence of an external field, the total electronic energy may now be written as

$$E[\rho(\boldsymbol{\kappa})] = \sum_{pq} h_{pq} \tilde{D}_{pq}(\boldsymbol{\kappa}) + \frac{1}{2} \sum_{pqrs} (pq|rs) \tilde{D}_{pq}(\boldsymbol{\kappa}) \tilde{D}_{rs}(\boldsymbol{\kappa}) + E_{\text{xc}}[\rho(\boldsymbol{\kappa})] + V_{\text{NN}}, \quad (26)$$

where

$$h_{pq} = \int \phi_p^\dagger(\mathbf{r}) \hat{h}_D \phi_q(\mathbf{r}) d\mathbf{r} - \sum_K Z_K \int \frac{\Omega_{pq}(\mathbf{r})}{r_K} d\mathbf{r}, \quad (27)$$

$$(pq|rs) = \iint \frac{\Omega_{pq}(\mathbf{r}_1) \Omega_{rs}(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_1 d\mathbf{r}_2. \quad (28)$$

In the following, we shall consider the optimization of the energy written in the form eq. (26). However, it is first necessary to examine in some detail the functional form of the exchange–correlation term  $E_{\text{xc}}[\rho(\boldsymbol{\kappa})]$  in this expression.

We here restrict our attention to three kinds of exchange–correlation functionals. In the local density approximation (LDA), the exchange–correlation energy is calculated by integration over the energy density  $e_{\text{xc}}$ , which in this case is a local function of the electron density:

$$E_{\text{xc}}^{\text{LDA}}[\rho(\boldsymbol{\kappa})] = \int e_{\text{xc}}(\rho(\mathbf{r}, \boldsymbol{\kappa})) d\mathbf{r}. \quad (29)$$

In the generalized gradient approximation (GGA), the exchange–correlation energy density is a local function of the density and the norm of its gradient:

$$E_{\text{xc}}^{\text{GGA}}[\rho(\boldsymbol{\kappa})] = \int e_{\text{xc}}(\rho(\mathbf{r}, \boldsymbol{\kappa}), \zeta(\mathbf{r}, \boldsymbol{\kappa})) d\mathbf{r}, \quad (30)$$

where we have introduced

$$\zeta(\mathbf{r}, \boldsymbol{\kappa}) = \nabla \rho(\mathbf{r}, \boldsymbol{\kappa}) \cdot \nabla \rho(\mathbf{r}, \boldsymbol{\kappa}), \quad (31)$$

$$\nabla \rho(\mathbf{r}, \boldsymbol{\kappa}) = \sum_{pq} \tilde{D}_{pq}(\boldsymbol{\kappa}) \nabla \Omega_{pq}(\mathbf{r}). \quad (32)$$

Finally, in hybrid theories, some proportion of the Hartree–Fock exchange is included in the exchange–correlation energy:

$$\begin{aligned} E_{\text{xc}}^{\text{hybrid}}[\rho(\boldsymbol{\kappa})] &= E_{\text{xc}}^{\text{GGA}}[\rho(\boldsymbol{\kappa})] + \gamma E_{\text{x}}^{\text{HF}}[\rho(\boldsymbol{\kappa})] \\ &= E_{\text{xc}}^{\text{GGA}}[\rho(\boldsymbol{\kappa})] - \frac{1}{2} \gamma \sum_{pqrs} (pq|rs) \tilde{D}_{ps}(\boldsymbol{\kappa}) \tilde{D}_{rq}(\boldsymbol{\kappa}). \end{aligned} \quad (33)$$

For all three cases of Kohn–Sham DFT (i.e., LDA, GGA, and hybrid theories), we have now succeeded in writing the energy as an unconstrained function of the nonredundant elements of the orbital-rotation operator eq. (21).

The Kohn–Sham energy eq. (17) may now be optimized by invoking the minmax principle of Talman,<sup>21</sup> stating that the total energy corresponds to a minimum of  $E[\rho]$  with respect to rotations between occupied and virtual electronic orbitals and to a maximum with respect to rotations between occupied electronic orbitals and (unoccupied) positronic orbitals. We note that, in the nonrelativistic domain, by contrast, the optimized ground-state energy corresponds to a global minimum of the energy function—that is, to a minimum of  $E[\rho]$  with respect to *all* rotations between occupied and virtual orbitals.

### Expansion of the Kohn–Sham Energy

To optimize the Kohn–Sham energy, to calculate different kinds of molecular properties, and so on, it is necessary to determine the expansion of the energy eq. (26) to a given order in the orbital-rotation elements  $\kappa_{pq}$ . In the following, we shall expand the Kohn–Sham energy only to first order, as is sufficient for energy optimizations. We emphasize, however, that the scheme described here may be straightforwardly extended to higher orders.

Expanding the Kohn–Sham energy to first order, we obtain

$$E(\boldsymbol{\kappa}) = E[\rho(\boldsymbol{\kappa})] \Big|_{\boldsymbol{\kappa}=0} + \sum_{pq} \frac{\partial E[\rho(\boldsymbol{\kappa})]}{\partial \kappa_{pq}} \Big|_{\boldsymbol{\kappa}=0} \kappa_{pq} + \mathcal{O}(\boldsymbol{\kappa}^2)$$

$$= E^{[0]} + \sum_{pq} E_{pq}^{[1]} \kappa_{pq} + \mathcal{O}(\kappa^2), \quad (34)$$

where  $E^{[0]}$  is the zero-order energy and  $E_{pq}^{[1]}$  are elements of the electronic gradient calculated at  $\kappa = \mathbf{0}$ . To determine the derivatives of the energy eq. (34), we first perform a Baker–Campbell–Hausdorff (BCH) expansion of the density matrix eq. (24):

$$\tilde{D}_{pq} = \langle 0 | p^\dagger q | 0 \rangle + \sum_{rs} \langle 0 | [r^\dagger s, p^\dagger q] | 0 \rangle \kappa_{rs} + \mathcal{O}(\kappa^2). \quad (35)$$

The derivatives may then be identified by inserting this expansion in the expression for the energy eq. (26) and comparing terms to the same order in  $\kappa_{pq}$ . This procedure is straightforward for the first and second terms in eq. (26), but the exchange–correlation term warrants special attention.

To determine the  $\kappa$  dependence of the exchange–correlation term, we first BCH expand the density and its gradient in  $\kappa$ :

$$\begin{aligned} \rho(\kappa) &= \rho_0 + \sum_{pqrs} \langle 0 | [r^\dagger s, p^\dagger q] | 0 \rangle \Omega_{pq} \kappa_{rs} + \mathcal{O}(\kappa^2); \\ \rho_0 &= \sum_{pq} \Omega_{pq} \langle 0 | p^\dagger q | 0 \rangle, \end{aligned} \quad (36)$$

$$\begin{aligned} \zeta(\kappa) &= \zeta_0 + 2 \sum_{pqrs} \langle 0 | [r^\dagger s, p^\dagger q] | 0 \rangle (\nabla \rho_0 \cdot \nabla \Omega_{pq}) \kappa_{rs} + \mathcal{O}(\kappa^2); \\ \zeta_0 &= \nabla \rho_0 \cdot \nabla \rho_0. \end{aligned} \quad (37)$$

Next, by expanding the exchange–correlation energy density of eq. (30) and inserting eqs. (36) and (37), we find

$$\begin{aligned} e_{xc}(\rho, \zeta) &= e_{xc}(\rho_0, \zeta_0) + \sum_{rs} \left( \frac{\partial e_{xc}}{\partial \rho} \frac{\partial \rho}{\partial \kappa_{rs}} + \frac{\partial e_{xc}}{\partial \zeta} \frac{\partial \zeta}{\partial \kappa_{rs}} \right) \Big|_{\kappa=0} \kappa_{rs} + \mathcal{O}(\kappa^2) \\ &= e_{xc}(\rho_0, \zeta_0) + \sum_{pqrs} \langle 0 | [r^\dagger s, p^\dagger q] | 0 \rangle \\ &\quad \times \left( \frac{\partial e_{xc}}{\partial \rho} \Omega_{pq} + 2 \frac{\partial e_{xc}}{\partial \zeta} \nabla \rho_0 \cdot \nabla \Omega_{pq} \right) \kappa_{rs} + \mathcal{O}(\kappa^2). \end{aligned} \quad (38)$$

Substituting this result in eq. (30), we obtain the expansion of the GGA exchange–correlation energy in  $\kappa$ . *Mutatis mutandis*, the same method may be used for non-GGA functionals. In particular, for the LDA exchange–correlation energy eq. (29), there is no contribution from the density gradient; for hybrid functionals, the contribution from the Hartree–Fock exchange is obtained by inserting the expansion for the density matrix eq. (35) in the Hartree–Fock exchange contribution to eq. (33).

Comparing terms to different orders, we obtain the following expressions for the energy and for the gradient elements:

$$\begin{aligned} E^{[0]} &= \sum_i h_{ii} + \frac{1}{2} \sum_{ij} [(ii|jj) - \gamma(ij|ji)] \\ &\quad + \int e_{xc}(\rho_0, \zeta_0) d\mathbf{r} + V_{NN}, \end{aligned} \quad (39)$$

$$E_{ia}^{[1]} = \frac{\partial E}{\partial \kappa_{ai}^*} \Big|_{\kappa=0} = E_{ai}^{[1]*} \quad (40)$$

$$\begin{aligned} &= -h_{ia} - \sum_j [(ia|jj) - \gamma(ij|ja)] \\ &\quad - \int \left( \frac{\partial e_{xc}}{\partial \rho} \Big|_0 \Omega_{ia} + 2 \frac{\partial e_{xc}}{\partial \zeta} \Big|_0 \nabla \rho_0 \cdot \nabla \Omega_{ia} \right) d\mathbf{r}, \end{aligned} \quad (41)$$

In accordance with the expansion of the wave function in nonredundant parameters eq. (22), the only elements of the gradient are  $E_{ai}^{[1]}$  and  $E_{ia}^{[1]}$ .

By partial integration, it is possible to reexpress the electronic gradient eq. (41) in terms of the exchange–correlation potential

$$\hat{v}_{xc} = \frac{\delta E_{xc}}{\delta \rho} = \frac{\partial e_{xc}}{\partial \rho} - \nabla \cdot \frac{\partial e_{xc}}{\partial \nabla \rho} \quad (42)$$

to yield

$$E_{ia}^{[1]} = -h_{ia} - \sum_j [(ia|jj) - \gamma(ij|ja)] - \int \hat{v}_{xc} \Omega_{ia} d\mathbf{r}. \quad (43)$$

However, for gradient-corrected functionals, the explicit integration over the exchange–correlation potential may require the calculation of the Laplacian of the density or the full Hessian of the density at each Gaussian quadrature point. The computationally less expensive form given as the last term of eq. (41), which is usually obtained from eq. (43) by partial integration, arises automatically in our formalism.

### Optimization of the Kohn–Sham Energy

A set of necessary conditions for an optimal Kohn–Sham energy is obtained by setting the elements of the gradient equal to zero:

$$E_{ia}^{[1]} = 0. \quad (44)$$

Several schemes of numerical analysis such as Newton’s method and any of its globally convergent modifications may be invoked to solve these equations. However, probably the most useful approach is obtained by recognizing that the elements of the electronic gradient eq. (41) correspond to the off-diagonal elements of the Kohn–Sham matrix:

$$E_{ia}^{[1]} = -F_{ia}, \quad (45)$$



$$F_{pq} = h_{pq} + \sum_j [(pq|jj) - \gamma(pj|jq)] + \int \hat{v}_{xc} \Omega_{pq} d\mathbf{r}. \quad (46)$$

Conventional diagonalization of the Kohn–Sham matrix therefore ensures that the conditions eq. (44) are satisfied. However, because the Kohn–Sham matrix eq. (46) depends on the canonical orbitals produced by its diagonalization, the solution cannot be obtained in a single step. Rather, we must repeatedly construct and diagonalize the Kohn–Sham matrix until the orbitals produced by its diagonalization are identical to the orbitals used for its construction. A self-consistent field (SCF) has then been established, and the iterations are terminated.

In relativistic theory, the Kohn–Sham operator is unbounded from below. In order that the Kohn–Sham iterations produce bound electronic solutions and do not lead to a variational collapse, care must be exercised in the design of the atomic-orbital (AO) basis set. By constructing the basis as a direct product of a primary nonrelativistic basis for the large components and a secondary basis for the small components (generated from the large-component basis by invoking the principle of kinetic balance), electronic solutions are obtained by diagonalization of the relativistic Kohn–Sham matrix. Furthermore, at each SCF iteration, the density matrix is constructed from the lower electronic solutions. This approach corresponds to the use of projection operators based on the current mean-field potential in the Furry bound-interaction picture, as suggested by Mittleman.<sup>22</sup>

## Implementation

The DFT implementation reported in this article forms an extension to the Hartree–Fock module of the DIRAC code<sup>15</sup> for four-component relativistic molecular calculations. An exciting aspect of this implementation is that the DIRAC Hartree–Fock module has an extensive functionality, which can be readily adapted to Kohn–Sham calculations. In addition to energy calculations, the Hartree–Fock module allows the calculation of molecular gradients for use in geometry optimizations; furthermore, expectation values, linear and quadratic response functions, as well as one-photon excitation energies and transition moments may be calculated. A general setup exists for the definition of one-electron property operators, limited only by what integrals can be calculated by the integral module HERMIT.<sup>23</sup> The current integral list of HERMIT features about fifty one-electron integrals. In addition, the Fock and Kohn–Sham matrix construction of DIRAC is fully parallelized under MPI, using an efficient integral-screening algorithm.<sup>24</sup>

The DIRAC code utilizes a scheme that provides the maximum point-group and time-reversal symmetries of  $D_{2h}$  and its subgroups.<sup>25</sup> Time-reversal symmetry is handled by the use of quaternion algebra, thereby reducing the generally complex four-component Hartree–Fock/Kohn–Sham equations to quaternion two-component form. The large and small components of the resulting quaternion two-component Kramers orbitals are separately expanded in a real (Gaussian) basis

$$\begin{aligned} \mathcal{O}\psi_k &= \begin{bmatrix} \mathcal{O}\psi_k^L \\ \mathcal{O}\psi_k^S \end{bmatrix} = \begin{bmatrix} \chi^L & 0 \\ 0 & \chi^S \end{bmatrix} \begin{bmatrix} \mathcal{O}\mathbf{c}_k^L \\ \mathcal{O}\mathbf{c}_k^S \end{bmatrix}; \\ \mathcal{O}\mathbf{c}_k^X &= \mathbf{c}_{0k}^X + \mathfrak{i}\mathbf{c}_{1k}^X + \mathfrak{j}\mathbf{c}_{2k}^X + \mathfrak{k}\mathbf{c}_{3k}^X; (X = L, S). \end{aligned} \quad (47)$$

where  $\chi^L$  and  $\chi^S$  are vectors containing the basis functions of the large and small components, respectively, and  $\mathbf{c}_k$  are vectors of the corresponding quaternion expansion coefficients, spanned by the quaternion unit vectors  $\mathfrak{i}$ ,  $\mathfrak{j}$ , and  $\mathfrak{k}$ . By invoking spatial symmetry, further symmetry reduction is manifested by reduction to complex algebra for the groups  $C_s$ ,  $C_2$ , and  $C_{2h}$ , and to real algebra for the groups  $D_2$ ,  $C_{2v}$ , and  $D_{2h}$ .

The four-component DFT implementation reported in this article is based on a recent nonrelativistic implementation of DFT in the DALTON code.<sup>26</sup> The present DIRAC–DALTON DFT implementation is, in turn, partly based on that of CADPAC,<sup>27</sup> using the same routines for the LDA and GGA functionals and a stripped-down (no-symmetry) version of the CADPAC routines for generating abscissas and weights for the numerical integration. Our implementation of four-component Kohn–Sham theory currently supports three functionals: the LDA functional,<sup>28,29</sup> the gradient-corrected BLYP (Becke–Lee–Yang–Parr) functional,<sup>30,31</sup> and the hybrid functional B3LYP (three-parameter hybrid BLYP).<sup>32,33</sup>

The numerical integration scheme<sup>34</sup> is based on the Becke partitioning<sup>35</sup> of the molecular volume into atomic ones, for which the quadrature is performed in spherical coordinates. To reduce computational cost, the grid points are restricted to symmetry-independent atoms

$$I = \int f(\mathbf{r}) d\mathbf{r} = \sum_A g(A) I_A; \quad I_A = \int f_A(\mathbf{r}) d\mathbf{r}, \quad (48)$$

where  $g(A)$  is the multiplicity of the symmetry-independent center  $A$ . A further symmetry reduction is obtained by constructing the density and its derivatives in the symmetry-adapted AO basis, giving rise to symmetry blocking. We have replaced the Euler–MacLaurin radial quadrature of CADPAC by the radial quadrature proposed by R. Lindh et al.,<sup>36</sup> which gives better integrated densities with fewer radial points. On the other hand, we have retained the Lebedev 2D angular quadrature of CADPAC. The numerical integration has been parallelized under MPI by distributing the grid points on nodes.

## A Study of Au<sub>2</sub> and Isoelectronic Species

The gold dimer Au<sub>2</sub> has been the subject of numerous experimental studies, both in the gas phase and in the matrix. Au<sub>2</sub> and its lighter homologs Cu<sub>2</sub> and Ag<sub>2</sub> are electronically the simplest transition-metal dimers, with no open  $d$  subshells, and constitute the starting point for studies of transition-metal clusters of interest in catalysis and thin-film growth.<sup>37</sup> However, because of the relativistic contraction of  $6s$  orbitals and the concomitant expansion of the  $5d$  orbitals, the contributions from the  $(n - 1)d$  orbitals to the bonding may be significant, unlike for its lighter homologs. These strong relativistic effects combine to give a bond length of Au<sub>2</sub> between those of Cu<sub>2</sub> and Ag<sub>2</sub>.<sup>3</sup> From a computa-

tional point of view,  $\text{Au}_2$  has served as an important test case for relativistic methods—see, for example, refs. <sup>38</sup> and <sup>59</sup>. In particular, we here note that relativistic four-component DFT calculations on  $\text{Au}_2$  have been reported by Liu and van Wüllen,<sup>39</sup> by Varga et al.,<sup>13,40</sup> and very recently by Yanai et al.<sup>14</sup>

Although unknown in the gas phase, the isoelectronic species  $\text{Hg}_2^{2+}$  plays a key role in the aqueous chemistry of mercury. Very few theoretical studies have been reported for this system;<sup>41–45</sup> see also the discussion in ref. <sup>46</sup>. They all yield negative dissociation energies in the gas phase, but the large spread in the calculated spectroscopic constants (partly due to the use of small basis sets) makes a comparison with our results difficult.

As a first application of our DFT implementation, we have calculated spectroscopic constants of  $\text{Au}_2$ ,  $\text{Hg}_2^{2+}$ , and the isoelectronic species  $\text{HgAu}^+$  and  $\text{HgPt}$ . In the course of our studies, we have also included  $\text{AuH}$ . The  $\text{HgAu}^+$  cation,  $\text{Au}_2$ , and the isoelectronic anion  $\text{PtAu}^-$  have been studied by Wesendrup et al.<sup>38</sup> We are aware of no theoretical or experimental investigations of  $\text{HgPt}$ .

### Computational Details

For the Pt, Hg, and Au atoms, we used uncontracted  $24s20p14d10f$  dual-family Gaussian basis sets. The Au basis set is that of ref. <sup>47</sup> but with the two outer *s* exponents replaced by an even-tempered series of four functions (ratio 2.5). The final basis is identical to that used by Wesendrup et al.<sup>38</sup> at the four-component level, except that we did not modify the core functions. The basis sets for Pt and Hg were constructed in a similar manner.<sup>48</sup> For hydrogen, we used the aug-cc-pVTZ basis set of Dunning<sup>49</sup> in uncontracted form.

All calculations were carried out with Gaussian nuclear charge distributions.<sup>50</sup> The exchange–correlation functionals were used in a self-consistent manner and in their spin-independent forms. We employed the simple Coulombic correction proposed by Visscher;<sup>51</sup> it has been shown to model very well the contribution of (SS|SS) integrals to spectroscopic constants, thus eliminating their calculation.

The spectroscopic constants were obtained by second-order perturbation theory, starting from the harmonic approximation, thus including the effects of cubic anharmonicity to second order and those of quartic anharmonicity to first order. The necessary derivatives of the potential-energy curves were obtained from polynomial fits. To get stable values of the anharmonicities, we found it necessary to do sixth-order fits of seven points within the first harmonic standard deviation. We have not calculated dissociation energies as our use of functionals dependent on the density rather than the spin density is likely to result in overbinding, as pointed out by Liu and van Wüllen<sup>52</sup> and by Varga et al.<sup>13</sup>

### Results and Discussion

Our results are summarized in Table 1. All species show a minimum although that of  $\text{Hg}_2^{2+}$  is known to be a local one. Our results for  $\text{Au}_2$  and  $\text{HgAu}^+$  can be compared directly with the scalar relativistic pseudopotential (SRPP) results of Wesendrup et al.,<sup>38</sup> obtained with a similar basis (DZ + *f* polarization). Whereas our LDA bond lengths and harmonic frequencies tend to agree with

their MP2 results, our GGA and hybrid results are more in line with their coupled-cluster results.

For  $\text{Au}_2$ , Mayer et al. have demonstrated that relativistic corrections to the exchange–correlation functionals [as calculated at the second-order Douglas-Kroll (DK2) level] have a negligible effect on the spectroscopic constants;<sup>53</sup> their results were confirmed at the four-component level by Varga et al.<sup>13,40</sup> At the LDA level, there is an excellent agreement among the results obtained with the zeroth-order regular approximation (ZORA) Hamiltonian,<sup>54</sup> with the DK2 Hamiltonian,<sup>53</sup> and with the four-component Dirac–Coulomb Hamiltonian (ref. <sup>39</sup> and our results). The DK2 Hamiltonian was used in the spinfree form; as shown by van Lenthe et al., the spin-orbit effects on the spectroscopic constants of  $\text{Au}_2$  are small.<sup>55</sup>

At the GGA level, there is again a good agreement for all three Hamiltonians with the B88P86 functional,<sup>30,56</sup> whereas our use of the BLYP functional leads to a longer bond and a lower harmonic frequency, in excellent agreement with the results of Yanai et al.<sup>14</sup> The B3LYP functional modifies the BLYP result only slightly—indeed, the best agreement with experiment is obtained with the LDA functional.

Liu and van Wüllen have attributed the better performance of LDA for  $\text{Au}_2$  to the fact that the *5d* dispersion interaction is unaccounted for by density functionals.<sup>52</sup> However, even though the dispersion is particularly strong between gold atoms—the aurophilic interaction<sup>57</sup>—it is likely to be swamped by the much stronger covalent interaction in the bonding region. To check this, we have calculated the spectroscopic constants of  $\text{AuH}$ , where dispersion does not contribute. Again, the LDA functional agrees better with experiment than do the GGA and hybrid functionals, although the difference is smaller.

Varga et al. conclude that LDA is the better functional in that it gives more realistic bond lengths for heavy-element species.<sup>13,58</sup> However, this statement should be viewed with some caution as the right answer may occur by cancellation of error, one possible source of error arising from the basis set.

Van Lenthe et al. find that a larger basis leads to only minor modifications of the spectroscopic constants of  $\text{Au}_2$ ;<sup>54</sup> however, these authors did not include *g* functions. Hess and Kaldor have shown that the inclusion of *g* functions as well as the counterpoise-correction is important for  $\text{Au}_2$ .<sup>59</sup> Upon adding four *g* functions to the Au basis in the same range as those of Wesendrup et al.,<sup>38</sup> we find that the bond length of  $\text{Au}_2$  is reduced from 254.5 to 253.7 pm at the BLYP level, indicating that basis-set effects are not sufficient to explain the discrepancies of our results with respect to experiment. It also is worth recalling that the basis-set requirements are different for the two methods: in coupled-cluster theory, the orbitals are used to construct a highly correlated wave function; in DFT, they are used to construct a density. An illuminating discussion of this point has been given by Baerends and Gritsenko.<sup>60</sup>

Another source of error are the functionals themselves—their mathematical form or their subsequent parametrization. The GGA functionals have generally been parametrized for light elements, for which LDA leads to a pronounced overbinding. For transition metals, the overbinding of LDA is less severe, and GGAs tend to give too weak binding. Some impression of the performance of the various functionals can be extracted from Table 2, where the extent



**Table 1.** Bond Lengths ( $r_e$ , in pm), Harmonic Frequencies ( $\omega_e$ , in  $\text{cm}^{-1}$ ) and Anharmonicities ( $\omega_e x_e$ , in  $\text{cm}^{-1}$ ).

Molecule	Hamiltonian	Method	Ref.	$r_e$	$\omega_e$	$\omega_e x_e$
Au <sub>2</sub>	DC	HF	tw	259.3	159.2	0.36
		LDA	tw	245.0	195.6	0.18
		LDA	39	245.4	196	
		B88P86	39	251.3	183	
		BLYP	tw	254.5	169.3	0.60
		BLYP	14	254.9	173	
	DK2	B3LYP	tw	253.5	172.9	0.50
		LDA	53	245.5	193	
		B88P86	53	251.4	178	
		MP2	59	241.8	212.4	
		CCSD	59	247.7	192.7	
		CCSD(T)	59	247.0	194.3	
	ZORA	LDA	54	245.3	197	
		B88P86	54	251.3	178	
	SRPP	MP2	38	245.4	205	
		CCSD	38	251.0	185	
		CCSD(T)	38	250.5	182	0.47
		exp	61	247.2	191	0.42
Hg <sub>2</sub> <sup>2+</sup>	DC	HF	tw	269.5	136.9	0.26
		LDA	tw	258.7	145.0	0.58
		BLYP	tw	273.1	112.3	0.50
		B3LYP	tw	269.0	124.3	0.25
HgAu <sup>+</sup>	DC	HF	tw	267.6	125.3	0.39
		LDA	tw	249.4	174.9	0.46
		BLYP	tw	260.8	142.1	0.58
		B3LYP	tw	259.7	145.6	0.59
	SRPP	MP2	38	252.8	167	
		CCSD	38	259.0	147	
		CCSD(T)	38	258.1	139	0.39
		exp	61	247.2	191	0.42
HgPt	DC	HF	tw	269.1	105.6	0.77
		B3LYP	tw	255.3	154.3	0.77
AuH	DC	HF	tw	157.0	2097.7	33.1
		LDA	tw	152.5	2327.9	46.9
		BLYP	tw	154.3	2230.8	52.7
		B88P86	39	153.7	2259	
		B3LYP	tw	153.8	2249.1	47.6
		exp	61	152.4	2305	

The Hamiltonians cited are the four-component Dirac–Coulomb operator (DC), the second-order spin-free Douglas–Kroll Hamiltonian (DK2), the zeroth-order regular approximation Hamiltonian (ZORA), and the scalar relativistic pseudo-potential Hamiltonian (SRPP). In addition to our own results (tw), we have selected some results in the literature for comparison. tw = this work.

$\langle r^2 \rangle^{1/2}$  and energy of the  $5d$  and  $6s$  orbitals of mercury are presented.

On the one hand, the  $6s$  Kohn–Sham orbitals are more compact than their Hartree–Fock counterparts, in the order  $\text{LDA} < \text{BLYP} < \text{B3LYP} \ll \text{HF}$ ; on the other hand, the Kohn–Sham  $5d$  orbitals are larger than the corresponding HF orbitals:  $\text{HF} < \text{B3LYP} < \text{LDA} < \text{BLYP}$ . In conclusion, the DFT functionals tend to enhance the effect of relativity—that is, the  $6s$  contraction and the  $5d$  expansion. For the molecules, this behavior translates into a larger  $d$  contribution to bonding. At the HF level, the Au<sub>2</sub> highest occupied molecular orbital (HOMO) is a  $\sigma_g(1/2)$  orbital formed by the overlap of  $6s$  orbitals with a  $d$  contribution of only 2%

**Table 2.** The Extent  $\langle r^2 \rangle^{1/2}$  of the Valence Orbitals of the Mercury Atom for Various Four-Component Relativistic Methods.

	$5d_{3/2}$	$5d_{5/2}$	$6s_{1/2}$
HF	2.199 (−0.650)	2.309 (−0.574)	4.324 (−0.328)
LDA	2.255 (−0.412)	2.373 (−0.344)	4.060 (−0.262)
BLYP	2.258 (−0.399)	2.377 (−0.331)	4.114 (−0.250)
B3LYP	2.243 (−0.456)	2.360 (−0.387)	4.134 (−0.274)

Orbital energies are given in parentheses. All quantities are in atomic units.

(from Mulliken population analysis); at the B3LYP level, the  $d$  contribution increases to 29%. By contrast, at the LDA and BLYP levels, the HOMO is a *gerade* combination of  $5d$  orbitals in the  $\omega = 3/2$  symmetry, whereas the  $6s$  contributions are distributed over a number of lower-energy orbitals. Clearly, a Mulliken population analysis of individual orbitals should be viewed with some caution because the orbitals of a closed-shell species can be rotated into one another without changing the energy. Nevertheless, our observations indicate the more important bonding role attributed to  $5d$  orbitals at the DFT level.

In the isoelectronic species  $\text{Hg}_2^{2+}$ , the HOMO is a  $6s\sigma_{g1/2}$  orbital at all levels of theory, with the following  $d$  contributions: HF (2%) < B3LYP (6%) < BLYP (9%) < LDA (11%). When one mercury atom is replaced by gold or platinum, the relative shift of orbital energies leads to more  $5d$  interaction from the lighter atom. At the HF level, the HOMO of  $\text{HgAu}^+$  is 68%  $6s(\text{Hg})$ , 20%  $6s(\text{Au})$  and 6%  $5d(\text{Au})$ . At the B3LYP level, the contributions change to 24, 17, and 56%, respectively; finally, at the LDA and BLYP levels, the HOMO is essentially  $5d_{5/2,5/2}(\text{Au})$ .

For  $\text{HgPt}$ , the HOMO is essentially  $5d_{5/2,5/2}(\text{Pt})$  at the B3LYP level; at the HF level, we converge to a state with a HOMO that is 32%  $6s(\text{Hg})$ , 23%  $6s(\text{Pt})$ , and 44%  $5d(\text{Pt})$ , but when a full configuration–interaction calculation is performed in the space of the highest six occupied orbitals as well as the lowest occupied molecular orbital (LUMO), the lowest state becomes an open-shell state with  $\Omega = 3$ . At the LDA and BLYP levels, no convergence was obtained.

## Conclusion

In this article, we have presented an implementation of the four-component relativistic Kohn–Sham equations for molecular calculations and demonstrated its usefulness by applications to  $\text{Au}_2$  and its isoelectronic species  $\text{Hg}_2^{2+}$ ,  $\text{HgAu}^+$ ,  $\text{HgPt}$ . It is found that the  $5d$  Kohn–Sham orbitals play a more active role in bonding than do the corresponding Hartree–Fock orbitals. Furthermore, we find that, when one of the mercury atoms of  $\text{Hg}_2^{2+}$  is replaced by the lighter atoms Au and Pt, the increasing relative difference in orbital energies leads to an increased multiconfigurational character of the electronic ground state. The calculated bond lengths, harmonic, and anharmonic frequencies are in good agreement with available calculated and experimental data. Among the GGA functionals the B88P86 functional seems to perform better than BLYP, but a more systematic study of the performance of various functionals for molecules containing heavy atoms is clearly needed.

We have discussed the relevance of the Coulomb and Breit operators for the construction of relativistic functionals. In particular, we have argued that, if the Breit operator is omitted in the Hamiltonian operator, we may with impunity ignore current functionals in the DFT calculations. As the effect of relativistic corrections to standard nonrelativistic density functionals have been shown to be small for spectroscopic constants,<sup>13,40,53</sup> four-component Dirac–Coulomb calculations may thus be carried out using such density functionals. By introducing an exponential parameterization of the noninteracting Kohn–Sham reference determinant, we have developed a convenient nonredundant parametrization of the Kohn–Sham energy within the second-quantization formalism.

This formalism is well suited to the further development of four-component relativistic Kohn–Sham response theory.

## Acknowledgments

TS would like to acknowledge stimulating discussions with E. Engel and W. Liu. Grants of computing time from the Norwegian High Performance Computing Consortium (NOTUR) are gratefully acknowledged, as well as excellent support, in particular from Roy Dragseth at The High Performance Computing Program at the University of Tromsø.

## References

1. Mendeleev, D. J Russ Phys Chem Soc 1871, 3, 25.
2. Pyykkö, P. Chem Rev 1988, 88, 563.
3. Pyykkö, P.; Desclaux, J.-P. Acc Chem Res 1979, 12, 276.
4. Koch, W.; Holthausen, M. C. A Chemist's Guide to Density Functional Theory; Wiley–VCH: Weinheim, 2000.
5. Rajagopal, A. K.; Callaway, J. Phys Rev B 1973, 7, 1912.
6. Hohenberg, P.; Kohn, W. Phys Rev B 1964, 136, 864.
7. Rajagopal, A. K. J Phys C 1978, 11, L943.
8. MacDonald, A. H.; Vosko, S. H. J Phys C Solid State Phys 1979, 12, 2977.
9. Engel, E.; Dreizler, R. M. Top Curr Chem 1996, 181, 1.
10. Engel, E.; Müller, H.; Speicher, C.; Dreizler, R. M. In Density Functional Theory; NATO ASI Series. Series B: Physics Vol. 337; Gross, E. K. U.; Dreizler, R. M., Eds.; Plenum: New York, 1995.
11. van Wüllen, C. J Comp Chem 1999, 20, 51.
12. Liu, W. J.; Hong, G. Y.; Dai, D. D.; Li, L. M.; Dolg, M. Theor Chem Acc 1997, 96, 75.
13. Varga, S.; Fricke, B.; Nakamatsu, H.; Mukoyama, T.; Anton, J.; Geschke, D.; Heitmann, A.; Engel, E.; Bastug, T. J Chem Phys 2000, 112, 3499.
14. Yanai, T.; Iikura, H.; Nakajima, T.; Ishikawa, Y.; Hirao, K. J Chem Phys 2001, 115, 8267.
15. Dirac, a relativistic *ab initio* electronic structure program, Release 3.2 (2000), written by T. Saue, V. Bakken, T. Enevoldsen, T. Helgaker, H. J. Aa. Jensen, J. K. Laerdahl, K. Ruud, J. Thyssen, and L. Visscher (<http://dirac.chem.sdu.dk>).
16. Saue, T. PhD thesis, University of Oslo, 1996.
17. Visser, O.; Visscher, L.; Aerts, P. J. C.; Nieuwpoort, W. C. Theor Chim Acta 1992, 81, 405.
18. Visscher, L.; Saue, T.; Nieuwpoort, W. C.; Fægri, K.; Gropen, O. J Chem Phys 1993, 99, 6704.
19. Gell–Mann, M. Nuovo Cimento Suppl 1956, 4, 848.
20. McWeeny, R.; Sutcliffe, B. T. Methods of Molecular Quantum Mechanics; Academic Press: London, 1976.
21. Talman, J. D. Phys Rev Lett 1986, 57, 1091.
22. Mittleman, M. H. Phys Rev A 1981, 24, 1167.
23. Hermit, a Gaussian molecular integrals package, written by T. Helgaker with contributions from K. Ruud, T. Saue, and P. Taylor.
24. Saue, T.; Fægri, K.; Helgaker, T.; Gropen, O. Mol Phys 1997, 91, 937.
25. Saue, T.; Jensen, H. J. Aa. J Chem Phys 1999, 111, 6211.
26. Dalton, release 1.0 (1997), an *ab initio* electronic-structure program, written by T. Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, K. Ruud, and H. Ågren, with contributions from T. Andersen, K. L. Bak, V. Bakken, O. Christiansen, P. Dahle, E. K. Dalskov, T. Enevoldsen, B. Fernandez, H. Heiberg, H. Hettema, D. Jonsson, S. Kirpekar, R. Kobayashi, H. Koch, K. V. Mikkelsen, P. Norman, M. J. Packer, T.

- Saue, P. R. Taylor, and O. Vahtras (<http://www.kjemi.uio.no/software/dalton>).
27. CADPAC: The Cambridge Analytical Derivative Package Issue 6, Cambridge 1995. A suite of quantum chemistry programs developed by R. D. Amos with contributions from I. L. Alberts, J. S. Andrews, S. M. Colwell, N. C. Handy, D. Jayatilaka, P. J. Knowles, R. Kobayashi, K. E. Laidig, G. Larning, A. M. Lee, P. E. Maslen, C. W. Murray, J. E. Rice, E. D. Simandiras, A. J. Stone, M.-D. Su, and D. J. Tozer.
28. Dirac, P. A. M. *Proc Cambridge Philos Soc* 1930, 26, 376.
29. Vosko, S. J.; Wilk, L.; Nusair, M. *Can J Phys* 1980, 58, 1200.
30. Becke, A. D. *Phys Rev A* 1988, 38, 3098.
31. Lee, C.; Yang, W.; Parr, R. G. *Phys Rev B* 1988, 37, 785.
32. Becke, A. D. *J Chem Phys* 1993, 98, 5648.
33. Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J Phys Chem* 1994, 98, 11623.
34. Murray, C. W.; Handy, N. C.; Laming, G. J. *Mol Phys* 1993, 78, 997.
35. Becke, A. D. *J Chem Phys* 1988, 88, 2547.
36. Lindh, R.; Malmqvist, P. Å.; Gagliardi, L. *Theor Chem Acc* 2001, 106, 178.
37. Morse, M. D. *Chem Rev* 1986, 86, 1049.
38. Wesendrup, R.; Laerdahl, J. K.; Schwerdtfeger, P. *J Chem Phys* 1999, 110, 9457.
39. Liu, W.; van Wüllen, C. *J Chem Phys* 1999, 110, 3730.
40. Varga, S.; Engel, E.; Sepp, W.-D.; Fricke, B. *Phys Rev A* 1999, 59, 4288.
41. Neisler, R. P.; Pitzer, K. S. *J Phys Chem* 1987, 91, 1084.
42. Ziegler, T.; Snijders, J. G.; Baerends, E. J. *J Chem Phys* 1981, 74, 1271.
43. Durand, G.; Spiegelmann, F.; Bernier, A. *J Phys B At Mol Phys* 1987, 20, 1161.
44. Strömberg, D.; Wahlgren, U. *Chem Phys Lett* 1990, 169, 109.
45. Ulvenlund, S.; Rosdahl, J.; Fischer, A.; Schwerdtfeger, P.; Kloos, L. *Eur J Inorg Chem* 1999, 1, 633.
46. Kaupp, M.; von Schnering, H. G. *Inorg Chem* 1994, 33, 4179.
47. Laerdahl, J. K.; Saue, T.; Fægri, K. *Theor Chem Acc* 1997, 97, 177.
48. Laerdahl, J. K. personal communication.
49. Dunning, T. H., Jr. *J Chem Phys* 1989, 90, 1007.
50. Visscher, L.; Dyall, K. G. *At Data Nucl Data Tables* 1997, 67, 207.
51. Visscher, L. *Theor Chem Acc* 1997, 98, 68.
52. Liu, W.; van Wüllen, C. *J Chem Phys* 2000, 113, 2506.
53. Mayer, M.; Häberlen, O. D.; Rösch, N. *Phys Rev A* 1996, 54, 4775.
54. van Lenthe, E.; Baerends, E. J.; Snijders, J. G. *J Chem Phys* 1994, 101, 9783.
55. van Lenthe, E.; Snijders, J. G.; Baerends, E. J. *J Chem Phys* 1996, 105, 6505.
56. Perdew, J. P. *Phys Rev B* 1986, 33, 8800.
57. Pyykkö, P. *Chem Rev* 1997, 97, 597.
58. Varga, S.; Fricke, B.; Nakamatsu, H.; Mukoyama, T.; Anton, J.; Geschke, D.; Heitmann, A.; Engel, E.; Bastug, T. *J Chem Phys* 2000, 113, 2508.
59. Hess, B. A.; Kaldor, U. *J Chem Phys* 2000, 112, 1809.
60. Baerends, E. J.; Gritsenko, O. V. *J Phys Chem A* 1997, 101, 5383.
61. Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure Constants of Diatomic Molecules*; Van Nostrand: New York, 1979.