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# Geometry optimizations in the zero order regular approximation for relativistic effects

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Analytical expressions are derived for the evaluation of energy gradients in the zeroth order regular approximation (ZORA) to the Dirac equation. The electrostatic shift approximation is used to avoid gauge dependence problems. Comparison is made to the quasirelativistic Pauli method, the limitations of which are highlighted. The structures and first metal-carbonyl bond dissociation energies for the transition metal complexes  $W(CO)_6$ ,  $Os(CO)_5$ , and  $Pt(CO)_4$  are calculated, and basis set effects are investigated. © 1999 American Institute of Physics. [S0021-9606(99)30317-2]

## I. INTRODUCTION

In the present paper expressions are derived for the evaluation of energy gradients of the zeroth order regular approximation (ZORA) (Refs. 1–3) to the Dirac equation. The regular expansion, which leads to the ZORA Hamiltonian, remains valid even for a Coulombic potential. This is in contrast to the expansion that leads to the Pauli Hamiltonian, which is divergent for a Coulombic potential. Harriman<sup>4</sup> already used the regular expansion, but called it the modified partitioning of the Dirac equation. It was shown in Ref. 5, that the ZORA Hamiltonian is bounded from below for Coulombic potentials. Exact solutions for the hydrogenic ions were given and in Ref. 6 it was shown that the scaled ZORA energies in that case are exactly equal to the Dirac energies.

Bond energies can be calculated accurately with the ZORA method using the electrostatic shift approximation (ESA), described in Ref. 6. With this method geometry optimizations can be performed if bond energies for different geometries are compared. For diatomics this pointwise tracing of the energy surface is still manageable, but for polyatomic atoms it will be cumbersome. Therefore it is desirable to have analytic expressions for the energy gradients. We present in Sec. III of this paper the derivation of analytic energy derivatives within the framework of the ZORA ESA method. Section IV discusses the use of a frozen core and basis set requirements for ZORA calculations.

In Sec. VI results of geometry optimizations are presented for a series of small molecules (diatomics) employing the scalar relativistic (SR) ZORA method, i.e., without spin-orbit coupling. The results are compared with results obtained from a pointwise calculation of bond energies in the SR ZORA ESA method. The SR ZORA optimized geometries have also been obtained for  $W(CO)_6$ ,  $Os(CO)_5$ , and  $Pt(CO)_4$  and are compared with geometries obtained with a quasirelativistic method based on the Pauli Hamiltonian for the same compounds, both calculated in this work with various basis sets and published ones.<sup>7</sup> It is well known that the Pauli Hamiltonian containing the first order relativistic correction terms (Darwin, mass-velocity, and spin-orbit cou-

pling) is not bounded from below. One may nevertheless try to diagonalize the Pauli Hamiltonian in a restricted (valence) space. This is usually denoted as the quasirelativistic method.<sup>8</sup> In order to avoid variational collapse in the QR-Pauli method, frozen cores have to be employed. Before entering the comparison with the present results and following up on the discussion of the use of frozen cores in the ZORA method, we discuss in Sec. V the stability problems of the quasirelativistic Pauli method in relation to the choice of both core orthogonalization functions and valence basis sets.

Recently, van Wüllen<sup>9</sup> proposed a modification of the ZORA method, which uses a model potential in the ZORA kinetic energy operator. For this method, called ZORA (MP), he derived analytical expressions for the energy gradients. The purpose of the ZORA(MP) method was to eliminate the gauge dependence of the ZORA approach. However, we will show that a (small) gauge dependence problem still exists in this ZORA (MP) method, which is not present in the ZORA ESA method. Moreover, we will show that the analytical expressions for the energy gradients following from the ZORA ESA method are easier to evaluate than the expressions following from the ZORA (MP) method.

A different variationally stable relativistic method developed for atomic and molecular calculations by Hess<sup>10</sup> uses the Douglas-Kroll transformation.<sup>11</sup> A density-functional implementation has been provided by Knappe and Rösch,<sup>12</sup> with the implementation of analytical energy gradients by Nasluzov and Rösch.<sup>13</sup> These schemes rely on momentum space evaluation of integrals and require the assumption of completeness of the finite basis sets employed in practical calculations. It is an advantage of the ZORA approach that the required matrix elements can easily be evaluated without further approximations in schemes that rely on 3D numerical integration, see, e.g., Refs. 14 and 15, making this method very straightforwardly applicable to molecules.

Our implementation of the analytical gradients for ZORA is based on a modification of the implementation of energy gradients in the nonrelativistic<sup>16,17</sup> and the quasirelativistic case<sup>7</sup> in the Amsterdam density functional (ADF) program.<sup>18,15,19</sup>

In our calculations we will use density functional theory (DFT), employing the usual (nonrelativistic) density functionals for the exchange-correlation energy; local density functionals (LDA) with gradient correction (GGC) terms added, namely, the Becke correction for exchange<sup>20</sup> and the Perdew correction for correlation.<sup>21</sup>

## II. THE ZORA EQUATION

The ZORA equation is the zeroth order of the regular expansion of the Dirac equation. If only a time-independent electric field is present, the one-electron (SR) ZORA Kohn–Sham equations can be written in atomic units ( $\mathbf{p} = -i\nabla$ ) as

$$(V + T[V])\Psi_i = \epsilon_i \Psi_i, \quad (1)$$

with

$$T^{\text{zora}}[V] = \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{2c^2 - V} \boldsymbol{\sigma} \cdot \mathbf{p} = \mathbf{p} \cdot \frac{c^2}{2c^2 - V} \mathbf{p} + \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma} \cdot (\nabla V \times \mathbf{p}), \quad (2a)$$

$$T_{\text{SR}}^{\text{zora}}[V] = \mathbf{p} \cdot \frac{c^2}{2c^2 - V} \mathbf{p}. \quad (2b)$$

Here use is made of the identity,

$$(\boldsymbol{\sigma} \cdot \mathbf{a})(\boldsymbol{\sigma} \cdot \mathbf{b}) = \mathbf{a} \cdot \mathbf{b} + i \boldsymbol{\sigma} \cdot (\mathbf{a} \times \mathbf{b}) \quad (3)$$

for the Pauli spin matrices  $\boldsymbol{\sigma}$ . The effective molecular Kohn–Sham potential  $V$  used in our calculations is the sum of the nuclear potential, the Coulomb potential due to the total electron density, and the exchange-correlation potential, for which we will use nonrelativistic approximations. The ZORA kinetic energy operator  $T^{\text{zora}}$ , depends on the molecular Kohn–Sham potential. The scalar relativistic (SR) ZORA kinetic energy operator  $T_{\text{SR}}^{\text{zora}}$ , is the ZORA kinetic energy operator without spin–orbit coupling. This operator can be used in cases where spin–orbit coupling is not important. For convenience we will refer to the (SR) ZORA kinetic energy with  $T[V]$ .

In Ref. 22 it was observed that replacing the molecular potential by the sum of the potentials of the neutral spherical reference atoms  $V_{\text{SA}}$  in the kinetic energy operator is not a severe approximation, thus

$$T[V_{\text{SA}}] \approx T[V]. \quad (4)$$

This procedure was called the sum of atoms potential approximation (SAPA). This has the advantage that when the ZORA Kohn–Sham equations are solved self-consistently (SCF) using a basis set, one only needs to calculate the ZORA kinetic energy matrix once, instead of in every cycle in the SCF scheme if the full molecular potential is used.

An improved one-electron energy can be obtained by using the scaled ZORA energy expression<sup>6</sup>

$$\epsilon_i^{\text{scaled}} = \frac{E_i^{\text{zora}}}{1 + \langle \Psi_i | Q[V] | \Psi_i \rangle}, \quad (5)$$

with

$$Q^{\text{zora}}[V] = \boldsymbol{\sigma} \cdot \mathbf{p} \frac{c^2}{(2c^2 - V)^2} \boldsymbol{\sigma} \cdot \mathbf{p}, \quad (6a)$$

$$Q_{\text{SR}}^{\text{zora}}[V] = \mathbf{p} \cdot \frac{c^2}{(2c^2 - V)^2} \mathbf{p}. \quad (6b)$$

If, for example, SAPA is used for  $T[V]$  then the same approximation has to be used for  $Q[V]$ .

## III. GEOMETRY OPTIMIZATIONS WITH ZORA

In this section expressions are derived for the evaluation of energy gradients in the (SR) ZORA case. Next, the implementation in the ADF program system is briefly discussed.

### A. Derivation of energy gradients for the ZORA ESA energy

The difference in energy between a molecule and its constituting atoms (fragments)  $A$ , calculated according to the (SR) ZORA ESA method,<sup>6</sup> is

$$\begin{aligned} \Delta E^{\text{ESA}} = & \frac{1}{2} \sum_{A, B \neq A}^N \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \sum_i^{\text{occ}} \langle \Psi_i | T[V] | \Psi_i \rangle \\ & - \sum_A^N \int \frac{\rho(1) Z_A}{|\mathbf{R}_A - \mathbf{r}_1|} d1 + \frac{1}{2} \int \int \frac{\rho(1)\rho(2)}{r_{12}} d1 d2 \\ & + E_{\text{xc}}[\rho] - \sum_A^N \left( \sum_j^{\text{occ}} \langle \Phi_j^A | T[V] | \Phi_j^A \rangle \right. \\ & \left. - \int \frac{\rho^A(1) Z_A}{|\mathbf{R}_A - \mathbf{r}_1|} d1 + \frac{1}{2} \int \int \frac{\rho^A(1)\rho^A(2)}{r_{12}} d1 d2 \right. \\ & \left. + E_{\text{xc}}[\rho^A] \right), \quad (7) \end{aligned}$$

with

$$\rho = \sum_i^{\text{occ}} \Psi_i^\dagger \Psi_i, \quad (8a)$$

$$\rho^A = \sum_j^{\text{occ}} (\Phi_j^A)^\dagger \Phi_j^A, \quad (8b)$$

$\Psi_i$  is a molecular orbital, and  $\Phi_j^A$  is a fragment orbital. The energy difference  $\Delta E^{\text{ESA}}$  was derived from the difference in the scaled (SR) ZORA total energies. Note the occurrence of the same operator  $T[V]$ , containing the *molecular* potential  $V$  in both the molecular and atomic “kinetic energy” terms. This is a consequence of the combined use of the scaled ZORA method and the ESA approximation, cf. Ref. 6, and is crucial for avoiding gauge dependency problems as well as obtaining numerically stable energy differences. In Ref. 6 the scaled ZORA total energy was found to be very accurate in comparison with fully relativistic results.

Suppose the molecular potential  $V$  present in the kinetic energy operator  $T[V]$  does not depend on the molecular orbitals  $\Psi_i$ , as it is the case for SAPA, for example. We will call this potential  $V_{\text{fix}}$  (for SAPA  $V_{\text{fix}} = V_{\text{SA}}$ ). Now finding

the orthonormal orbitals  $\Psi_i$  which minimize the energy difference  $\Delta E^{\text{ESA}}$  is equivalent to solving the molecular one electron ZORA equations,

$$[V + T[V_{\text{fix}}]]\Psi_i = \epsilon_i \Psi_i. \quad (9)$$

An alternative is to first solve the one-electron (SR) ZORA equation (1) self-consistently with a potential  $V$  in the kinetic energy operator that does depend on the orbitals  $\Psi_i$ . Afterwards one can then fix this potential, and use this fixed potential  $V_{\text{fix}}$  in the kinetic energy operator in Eq. (7). One can then vary the orbitals  $\Psi_i$  in Eq. (7) to find the minimum, thus without changing  $V_{\text{fix}}$  in the kinetic energy operator, which is equivalent to finding the solutions of the ZORA one-electron equations that were already solved. In this sense the ZORA ESA energy is stationary with respect to orbital variations. The potential  $V_{\text{fix}}$ , however, still depends on the geometry of the molecule, which is important in the case of geometry optimizations.

In an atomic basis set expansion the ZORA molecular orbitals  $\Psi_i$  are expressed as a sum over coefficients times primitive atomic basis functions  $\chi_\nu$ , each centered at one particular nucleus,

$$\Psi_i = \sum_\nu C_{\nu i} \chi_\nu. \quad (10)$$

If we take the derivative of the energy difference Eq. (7) with respect to a nuclear displacement  $X_A$  of nucleus A, we have to take into account the change in the coefficients  $C_{\nu i}$  (indirect derivative) as well as the change in the atomic basis functions  $\chi_\nu$  themselves (direct derivative), due to the displacement. We will now assume that we have solved the one-electron (SR) ZORA equation (9) with optimal coefficients  $C_{\nu i}$ . As in the nonrelativistic case the indirect derivative can be transformed into a direct derivative<sup>23</sup>

$$\sum_i^{\text{occ}} \sum_\nu \frac{\partial \Delta E^{\text{ESA}}}{C_{\nu i}} \frac{\partial C_{\nu i}}{\partial X_A} = - \sum_i^{\text{occ}} 2\epsilon_i \left\langle \frac{\partial \Psi_i}{\partial X_A} \middle| \Psi_i \right\rangle, \quad (11)$$

where  $\partial \Psi_i / \partial X_A$  represents the direct derivative of  $\Psi_i$  with respect to  $X_A$ , thus

$$\frac{\partial \Psi_i}{\partial X_A} = \sum_\nu C_{\nu i} \frac{\partial \chi_\nu}{\partial X_A}. \quad (12)$$

The kinetic energy operator in Eq. (7) is the same for both the molecule and the constituting atoms (fragments), and contains the molecular potential. This is the only difference with a similar expression in the nonrelativistic case and it is important in the case of geometry optimizations, which we will now consider.

The difference in the kinetic energy between a molecule and its constituting atoms (fragments) A, calculated according to the (SR) ZORA ESA method is

$$\Delta T^{\text{ESA}}[V] = \sum_i^{\text{occ}} \langle \Psi_i | T[V] | \Psi_i \rangle - \sum_A \sum_j^N \langle \Phi_j^A | T[V] | \Phi_j^A \rangle, \quad (13)$$

with  $\Phi_j^A$  the fragment orbitals. For deep core states the  $\sum_A \sum_j \Phi_j^A$  runs over fragment orbitals  $\Phi_j^A$ , or with suitable symmetry adaptation, over symmetry combinations of frag-

ment orbitals that each match a corresponding molecular orbital  $\Psi_i$  which it very closely resembles. This molecular orbital formed by a combination of fragment orbitals we call  $\phi_i$ . In the same way we can also make molecular orbitals  $\phi_i$  from the valence fragment orbitals, but then it is no longer guaranteed that there are molecular orbitals  $\Psi_i$  that they closely resemble. We have to remember that the number of occupied molecular orbitals may be different from the total number of occupied fragment orbitals. However, we will assume that the number of occupied deep core levels is the same.

In a linear combination of atomic orbitals (LCAO) expansion the ZORA molecular orbitals  $\Psi_i$  can be expressed as a sum over single atomic contributions

$$\Psi_i = \sum_A^N \Psi_i^A, \quad (14a)$$

$$\Psi_i^A = \sum_{\nu \in A} C_{\nu i} \chi_\nu^A. \quad (14b)$$

As we did for  $\Psi_i$  we express  $\phi_i$  as a sum over single atomic contributions  $\phi_i^A$ . The molecular orbitals  $\phi_i$  are constructed in such a way that  $\phi_i^A$  only has a contribution of one of the fragment orbitals  $\Phi_j^A$  on fragment A. This means that we can write

$$\sum_A^N \sum_j^{\text{occ}} \langle \Phi_j^A | T[V] | \Phi_j^A \rangle = \sum_A^N \sum_i^{\text{occ}} \langle \phi_i^A | T[V] | \phi_i^A \rangle. \quad (15)$$

The direct derivative of the kinetic energy difference Eq. (13) with respect to a nuclear displacement  $X_A$  of nucleus A is

$$\begin{aligned} \frac{\partial \Delta T^{\text{ESA}}}{\partial X_A} &= \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] | \Psi_i^A \right\rangle + \sum_i^{\text{occ}} \left\langle \Psi_i \middle| \frac{\partial T[V]}{\partial X_A} \middle| \Psi_i \right\rangle \\ &\quad - \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \phi_i^A}{\partial X_A} \middle| T[V] | \phi_i^A \right\rangle \\ &\quad - \sum_i^{\text{occ}} \sum_B^N \left\langle \phi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \phi_i^B \right\rangle. \end{aligned} \quad (16)$$

The one-center contributions in this equation are

$$\begin{aligned} &\sum_i^{\text{occ}} 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] | \Psi_i^A \right\rangle + \sum_i^{\text{occ}} \sum_B^N \left\langle \Psi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \Psi_i^B \right\rangle \\ &\quad - \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \phi_i^A}{\partial X_A} \middle| T[V] | \phi_i^A \right\rangle - \sum_i^{\text{occ}} \sum_B^N \left\langle \phi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \phi_i^B \right\rangle \\ &= \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( - \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_B} \middle| \Psi_i^A \right\rangle + \left\langle \phi_i^A \middle| \frac{\partial T[V]}{\partial X_B} \middle| \phi_i^A \right\rangle \right. \\ &\quad \left. + \left\langle \Psi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \Psi_i^B \right\rangle - \left\langle \phi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \phi_i^B \right\rangle \right). \end{aligned} \quad (17)$$

For valence orbitals each term in itself is very small, since

$$\frac{\partial}{\partial X_B} \frac{c^2}{2c^2 - V} = \frac{c^2}{(2c^2 - V)^2} \frac{\partial V}{\partial X_B} \quad (18)$$

is of order  $c^{-2}$ , which means that each term in Eq. (17) is of order  $c^{-2}$ . Only for deep core levels these terms can be of importance (see also the end of this section), but for these deep core levels  $\Psi_i^A$  is very close to  $\phi_i^A$  and these terms will cancel each other. We therefore neglect these one-center terms altogether and we are left with

$$\begin{aligned} \frac{\partial \Delta T^{\text{ESA}}}{\partial X_A} &\approx \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] \middle| \Psi_i^B \right\rangle \right. \\ &\quad + 2 \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_A} \middle| \Psi_i^B \right\rangle \\ &\quad + 2 \left\langle \Psi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \sum_{C \neq A, B}^N \Psi_i^C \right\rangle \Bigg) \\ &= \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] \middle| \Psi_i^B \right\rangle \right. \\ &\quad - \left. \left\langle \Psi_i^A \middle| T[V] \middle| \frac{\partial \Psi_i^B}{\partial X_B} \right\rangle \right) \\ &\quad + \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_A} - \frac{\partial T[V]}{\partial X_B} \middle| \Psi_i^B \right\rangle \right. \\ &\quad \left. + 2 \left\langle \Psi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \sum_{C \neq A, B}^N \Psi_i^C \right\rangle \right). \end{aligned} \quad (19)$$

The matrix elements which include a derivative of the ZORA kinetic energy with respect to a nuclear displacement will be very small since they are of order  $c^{-2}$  and involve two-center integrals. We can therefore further approximate this expression by

$$\begin{aligned} \frac{\partial \Delta T^{\text{ESA}}}{\partial X_A} &\approx \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] \middle| \Psi_i^B \right\rangle \right. \\ &\quad \left. - \left\langle \Psi_i^A \middle| T[V] \middle| \frac{\partial \Psi_i^B}{\partial X_B} \right\rangle \right). \end{aligned} \quad (20)$$

This expression is simple to evaluate and obeys the translational invariance condition, which states that if the whole molecule is translated, the total energy does not change. We can compare this with the nonrelativistic expression for the gradient of the kinetic energy

$$\begin{aligned} \frac{\partial T^{\text{NR}}}{\partial X_A} &= \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T^{\text{NR}} \middle| \Psi_i \right\rangle \\ &= \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T^{\text{NR}} \middle| \Psi_i^B \right\rangle - \left\langle \Psi_i^A \middle| T^{\text{NR}} \middle| \frac{\partial \Psi_i^B}{\partial X_B} \right\rangle \right). \end{aligned} \quad (21)$$

The total derivative of the energy difference Eq. (7) with respect to a nuclear displacement  $X_A$  of nucleus  $A$  is

$$\begin{aligned} \frac{d \Delta E^{\text{ESA}}}{d X_A} &= \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| V + T[V] - \epsilon_i \middle| \Psi_i \right\rangle \\ &\quad + \sum_{B \neq A}^N \frac{Z_A Z_B (X_A - X_B)}{|\mathbf{R}_A - \mathbf{R}_B|^3} \\ &\quad - \int \frac{\rho(1) Z_A (X_A - x_1)}{|\mathbf{R}_A - \mathbf{r}_1|^3} d1 \\ &\quad + \sum_i^{\text{occ}} \sum_B^N \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_B} \middle| \Psi_i \right\rangle, \end{aligned} \quad (22)$$

since

$$\begin{aligned} &\sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] \middle| \Psi_i^B \right\rangle - \left\langle \Psi_i^A \middle| T[V] \middle| \frac{\partial \Psi_i^B}{\partial X_B} \right\rangle \right) \\ &= \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] \middle| \Psi_i \right\rangle + \sum_i^{\text{occ}} \sum_B^N \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_B} \middle| \Psi_i \right\rangle. \end{aligned} \quad (23)$$

Compared to a similar nonrelativistic expression there is an extra term

$$\sum_i^{\text{occ}} \sum_B^N \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_B} \middle| \Psi_i \right\rangle. \quad (24)$$

This term mimics the gradient of the interaction due to an effective small component density, which would be present if the Dirac equation was used.

We may compare Eq. (20) with a recently derived analytical expressions for the ZORA kinetic energy gradient in the ZORA (MP) method by van Wüllen,<sup>9</sup>

$$\begin{aligned} \frac{\partial T^{\text{ZORA(MP)}}}{\partial X_A} &= \sum_i^{\text{occ}} 2 \left\langle \frac{\partial \Psi_i^A}{\partial X_A} \middle| T[V] \middle| \Psi_i \right\rangle \\ &\quad + \sum_i^{\text{occ}} \left\langle \Psi_i \middle| \frac{\partial T[V]}{\partial X_A} \middle| \Psi_i \right\rangle. \end{aligned} \quad (25)$$

The major difference with the ZORA ESA method [see also Eq. (23)] are one-center contributions

$$\sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \Psi_i^B \middle| \frac{\partial T[V]}{\partial X_A} \middle| \Psi_i^B \right\rangle - \left\langle \Psi_i^A \middle| \frac{\partial T[V]}{\partial X_B} \middle| \Psi_i^A \right\rangle \right), \quad (26)$$

which are present in the ZORA (MP) method, but which are not present in the ZORA ESA method. These one-center contributions can cause problems if the model potential on atom  $A$  used in the ZORA (MP) method has a finite value in the core region of atom  $B$ , which depends on the distance between  $A$  and  $B$ . In this case the ZORA kinetic energy of the (deep) core orbitals on atom  $B$  will depend on the actual distance between  $A$  and  $B$ , even if these (deep) core orbitals do not change shape. This is the gauge dependence problem of ZORA, see also Ref. 6, which is solved if the ZORA ESA method is used. In the ZORA (MP) method the model potential of atom  $A$  is usually not so large at distances between  $A$  and  $B$  which are in the order of (or larger than) typical bond lengths between  $A$  and  $B$ . This means that in general the errors in the optimized geometries and bond energies will

also not be so very large. A rough estimate of this error in the bond energy is the value of the electrostatic shift  $\Delta$  in the model potential due to atom  $A$  at the position of atom  $B$  divided by  $2c^2$  and multiplied by the kinetic energy of atom  $B$ , if atom  $B$  is the heavy atom, since

$$T[V+\Delta] \approx T[V] + \Delta Q[V] \approx T[V] + \frac{\Delta}{2c^2} T[V]. \quad (27)$$

In Sec. VI we will attempt to quantify these errors in the ZORA (MP) method for a real molecule. Note that in the ZORA ESA method, presented in this article, these errors due to the gauge dependence problem do not occur.

## B. Implementation

The ADF program<sup>18,15,19</sup> is designed to perform electronic structure calculations on molecular systems. The one-electron equations arising in the Kohn–Sham formulation of density functional theory, are solved by self-consistent field calculations. In the calculations a Slater-type orbital (STO) basis set is used. To solve the relativistic ZORA Kohn–Sham equations matrix elements have to be evaluated that differ from the ones occurring in nonrelativistic (NR) theory. A characteristic element of the methodology embodied in the ADF program suite is the calculation of the matrix elements of the effective one-electron KS Hamiltonian by numerical integration. The matrix elements of the ZORA Hamiltonian can also straightforwardly be evaluated by such numerical integration. In the SR ZORA equations the only difference arises in the calculation of the kinetic energy matrix. When calculating bond energies, care has to be taken to obtain results that are correct (in view of the gauge dependency of the ZORA method) and numerically precise (in view of the limited precision of the numerical integration). Details on the calculation of bond energies using the ZORA ESA method can be found in Ref. 6.

Our implementation of the analytical gradients for ZORA is based on a modification of the implementation of energy gradients in the nonrelativistic<sup>16,17</sup> and quasirelativistic case<sup>7</sup> in the ADF program. The only difference between these methods is the calculation of the gradient of the kinetic energy. We implemented the gradient of the SR ZORA kinetic energy according to Eq. (20). For the evaluation of the potential in the “kinetic energy” operator we used the sum of atoms potential approximation (SAPA), thus

$$T_{\text{SR}}^{\text{ZORA}}[V_{\text{SA}}] = \mathbf{p} \cdot \frac{c^2}{2c^2 - V_{\text{SA}}} \mathbf{p}. \quad (28)$$

For SAPA we refer to Sec. II and Ref. 22. The calculation of the gradient of the full ZORA “kinetic energy,” which includes spin–orbit coupling, was not implemented.

With the help of partial integration the SR ZORA ESA kinetic energy gradient is calculated as [Eq. (20)],

$$\sum_{k=1}^3 \sum_i^{\text{occ}} \sum_{B \neq A}^N \left( \left\langle \frac{\partial^2 \Psi_i^A}{\partial X_A \partial x_k} \left| \frac{c^2}{2c^2 - V_{\text{SA}}} \right| \frac{\partial \Psi_i^B}{\partial x_k} \right\rangle - \left\langle \frac{\partial \Psi_i^A}{\partial x_k} \left| \frac{c^2}{2c^2 - V_{\text{SA}}} \right| \frac{\partial^2 \Psi_i^B}{\partial X_B \partial x_k} \right\rangle \right), \quad (29)$$

which means that we do not need to calculate the derivative of the potential in this expression. It is thus easier to evaluate than the expression for the kinetic energy gradient in the ZORA (MP) method, see Ref. 9, where one does need such derivatives of the potential.

## IV. BASIS SET REQUIREMENTS IN THE FROZEN CORE APPROXIMATION

In the ADF program suite the frozen core approximation is used routinely and can also be applied in the SR ZORA method (not yet with ZORA including spin–orbit coupling). The frozen core approximation in its currently implemented form<sup>18</sup> employs a basis set of  $N$  functions  $\chi_\mu$  (STO's in our case) that are explicitly orthogonalized onto the  $M$  frozen core orbitals  $\phi_k^{\text{core}}$ . The frozen core orbitals themselves are usually represented in an extensive basis set of STO's that are used in the separate atomic calculation in which the frozen core orbitals are generated. A different representation of the core orbitals is however also possible, for instance by basis set free “numerical” atomic orbitals resulting from a Herman–Skilman type of numerical solution of the radial differential equation for the atomic orbitals. The set of basis functions  $\chi_\mu$  is now transformed into a set of core-orthogonal functions  $\bar{\chi}_\mu$  by forming a linear combination of each  $\chi_\mu$  with a set of core orthogonalization functions  $\chi_k^{\text{core}}$ , one for each core orbital,

$$\bar{\chi}_\mu = \chi_\mu + \sum_{k=1}^M \chi_k^{\text{core}} C_{k\mu}. \quad (30)$$

The coefficients  $C_{k\mu}$  are determined<sup>18</sup> from the  $N \times M$  orthogonality conditions

$$\langle \bar{\chi}_\mu | \phi_i^{\text{core}} \rangle = 0. \quad (31)$$

Using the overlap matrices  $S_{ki} = \langle \chi_k^{\text{core}} | \phi_i^{\text{core}} \rangle$  and  $R_{\mu i} = \langle \chi_\mu | \phi_i^{\text{core}} \rangle$  one obtains for the  $C$  coefficients the matrix equation

$$C = -RS^{-1}. \quad (32)$$

The secular equation for the determination of the valence electron orbitals is set up in the  $\bar{\chi}_\mu$  basis. The core orthogonalization functions may be considered to belong to the basis set but they do not represent degrees of freedom, their coefficients being fixed by the orthogonality conditions. They are usually functions that describe accurately the core wiggles of the valence orbitals. In fact, the exponents of the core orthogonalization functions are optimized, along with those of the valence basis functions, in atomic calculations, in such a way that the “valence” plus “core” sets give an optimal description of the *valence* atomic orbitals, including their core tails. It should be recognized, however, that if a single STO core orthogonalization function per core orbital (i.e., per core wiggle in the valence atomic orbital) is not considered a sufficiently accurate representation of the core wiggles, it is perfectly possible to incorporate into the set of functions  $\chi_\mu$  very contracted (core type) basis functions so as to improve the core part of the valence wave functions. The core orthogonality conditions simply determine a fixed number (equal to the number of core orbitals) of coefficients

in the total basis set expansion, irrespective of how many “valence” and “core” type basis functions it contains. As a matter of fact, given a total basis set, the results of the calculations are independent of which functions are chosen as the ones whose coefficients are to be fixed by the orthogonality conditions. We customarily choose, for reasons of numerical stability, from the total basis set as the core orthogonalization functions those that have maximum overlap with the core orbitals, so the matrix  $S$  above is as close as possible to the unit matrix.

In general the NR core orbitals are not the same as scalar relativistic ZORA core orbitals, which are again different from fully relativistic ZORA (including spin-orbit coupling) core orbitals. The basis set requirements for an accurate representation of the core part of the valence wave functions will also differ whether one uses NR, SR ZORA or ZORA. In the NR case the core wiggles of the valence functions can accurately be described by the core orthogonalization functions, such that one does not need additional corelike basis functions to get an accuracy of a few milliatomic units. On the other hand, in SR ZORA and ZORA one does need extra corelike basis functions, to get such high accuracy for the heavier systems. This is due to the fact that the core wiggles of especially the  $s$ -type valence electrons do not behave like Slater-type orbitals near the nucleus, but more like Dirac-type orbitals which are of the form

$$r^{\eta-1}e^{-\zeta r}, \quad (33)$$

where  $\eta$  does not have to be an integer. For STO's  $\eta$  is an integer.

In the SR ZORA case the frozen core approximation can be implemented in the same way as in the NR case, because one can use the same single group symmetry. The changes one has to make are in order of importance the following. The description of the core orbitals should come from SR ZORA atomic calculations (we generally use a SR ZORA version of an atomic STO basis set program). In the case of heavy atoms, the STO basis set in this atomic calculation cannot be kept identical to the NR STO basis set, but should, for high accuracy, be reoptimized and extended with extra core basis functions for the reasons indicated above. The basis sets for these atomic calculations, in which the (frozen) core orbitals are expressed also in the molecule, do not represent variational degrees of freedom in the SCF molecular calculations and need not be restricted for reasons of computational economy. The usually smaller basis sets for the molecular calculations are generated by optimizing them for the valence orbitals only. It is often (i.e., for light elements) sufficient to use one contracted basis function for each core wiggle of the accurately calculated SR ZORA valence orbital. The number of these functions is then equal to the number of core orbitals, and they can be used as the core orthogonalization functions of the basis set. The “valence” basis functions are of course optimized for the description of the outer part (valence region) of the valence orbitals. For the heavier atoms one also should add corelike basis functions, which are able to describe the core tail of the valence orbitals more accurately. In the SR ZORA case it is usually enough

TABLE I. Uranium scaled SR ZORA valence orbital energies in a.u. using the NR core description.

Basis set	6s	6p	5f	6d	7s
ADF IV	-1.600	-0.827	-0.126	-0.076	-0.125
ADF IV+1s 115	-3.605	-0.724	0.009	-0.024	-0.231

to add only one extra  $1s$ -type STO with large exponent  $\zeta$  to get an accuracy of a few milliatomic units in the atomic orbital energies.

In Table I we show, for the U atom, the effects if one uses NR core orbitals to orthogonalize upon in a SR ZORA calculation. If we use the standard ADF IV basis set (triple- $\zeta$  valence basis set) with a frozen core including the  $5d$  and all lower shells, the results still do not seem to be too bad [compared to the basis set free (“numerical”) all electron SR ZORA results of Table II]. However, if we add a  $1s$ -type STO with  $\zeta=115$  we see incipient variational collapse of the valence  $s$  orbital energies towards (although not yet anywhere near) a core orbital energy. This collapse is caused by admixing of core character, due to the orthogonalization on NR core orbitals, whereas one should have orthogonalized on SR ZORA core orbitals. The SR ZORA orbitals are in this case too different from the NR orbitals. This type of variational collapse, where valence levels acquire too low energies, is distinct from the variational instability of the Pauli Hamiltonian to be discussed in the next section.

In Table II we see the results for different basis sets if we use the correct orthogonalization on SR ZORA core orbitals. These results can be compared with the given numerically calculated all electron SR ZORA results. The standard (NR) ADF IV result is not very accurate. As expected, the addition of an extra  $1s$ -type STO with  $\zeta=115$  now does not lead to variational collapse. The accuracy on the other hand is still not high. We therefore have optimized the basis set, both the core orthogonalization functions and the other basis functions, to the valence SR ZORA orbitals. This optimized relativistic basis set, denoted BASREL, is of the same size as the ADF IV basis set. The results using basis set BASREL show a large improvement, especially (see the  $6s$  orbital energy) if one also adds an extra  $1s$ -type STO with  $\zeta=450$ . This enlarged basis set is able to give orbital energies with an accuracy better than 0.01 atomic units. We also give results using an extra  $2p$ -type STO with  $\zeta=150$ , which does not change the results much, showing that the wiggle of the SR ZORA valence  $6p$ -orbital can already be described to

TABLE II. Uranium scaled SR ZORA valence orbital energies in a.u. using the SR ZORA core description.

Basis set	6s	6p	5f	6d	7s
Numerical	-1.738	-0.830	-0.105	-0.064	-0.136
ADF IV	-1.537	-0.821	-0.169	-0.084	-0.121
ADF IV+1s 115	-1.593	-0.812	-0.156	-0.079	-0.125
BASREL	-1.677	-0.831	-0.117	-0.069	-0.131
BASREL+1s 450	-1.735	-0.823	-0.106	-0.065	-0.135
BASREL+1s 450+2p 150	-1.735	-0.823	-0.106	-0.065	-0.135

TABLE III. Uranium scaled ZORA valence orbital energies in a.u. using the SR ZORA core description.

'Basis set	$6s_{1/2}$	$6p_{1/2}$	$6p_{3/2}$	$5f_{5/2}$	$5f_{7/2}$	$6d_{3/2}$	$6d_{5/2}$	$7s_{1/2}$
Numerical	-1.718	-1.068	-0.741	-0.104	-0.074	-0.071	-0.054	-0.134
BASREL	-1.668	-1.057	-0.737	-0.121	-0.095	-0.075	-0.061	-0.129
BASREL+1s 450	-1.725	-1.048	-0.729	-0.110	-0.084	-0.071	-0.057	-0.133
BASREL+1s 450+2p 150	-1.714	-1.138	-0.733	-0.098	-0.072	-0.070	-0.056	-0.133

reasonable accuracy without an extra core like basis function.

If one wants to use the frozen core approximation in the ZORA case (including spin-orbit coupling) one should orthogonalize the basis functions on ZORA (spin-orbit coupled  $Y_{jm_j}$ ) core orbitals, which is not (yet) implemented in the ADF program system. One might wonder if using a SR ZORA core description would not be sufficient, since one expects the ZORA orbitals not to be very different from SR ZORA orbitals. In the spherical case for light atoms, the spin-orbit split (ZORA) eigenfunctions ( $j=l+1/2$  and  $j=l-1/2$ ) have almost the same radial behavior as the SR ZORA orbitals, the difference is then only in the spin and angular part. For closed shell cores then there is no difference whether one uses full ZORA or SR ZORA orbitals, because they span the same space. For heavier atoms, where spin-orbit coupling is important, this is no longer true. The radial behavior for the eigenfunctions in a Coulomb potential near the origin can be quite different for SR ZORA or ZORA orbitals. Especially the ZORA  $p_{1/2}$ -orbital differs from the SR ZORA  $p$ -orbital, because it has a mild singularity near the origin. We can perform the ZORA calculation with basis functions orthogonalized on SR ZORA core orbitals and investigate how large the error becomes. In Table III the results are given using the BASREL basis set. The accuracy is not so high (notably for the  $6s$ -orbital), we therefore add an extra  $1s$ -type STO with  $\zeta=450$  like before, which improves the results. Now we still do not have problems with variational collapse because  $s$ -orbitals are not affected by spin-orbit coupling, and the ZORA and SR ZORA  $s$ -orbitals are very close (the only difference is due to difference in the SCF potential). If we add an extra  $2p$ -type corelike STO with  $\zeta=150$  the use of a frozen SR  $2p$  core orbital rather than the proper  $2p_{1/2}$  orbital, shows up in a variational stability problem, the  $6p_{1/2}$  orbital energy is now 0.1 a.u. too low. This result will get worse if we add more corelike  $p$ -type STO's.

These results demonstrate the level of accuracy obtainable within the various procedures that can be adopted [NR, SR or full ZORA frozen cores; special relativistic (reoptimized) basis sets; introduction of extra corelike basis functions]. We conclude that the use of SR ZORA core orbitals and special relativistic basis sets, with one extra  $1s$  core function, represent a good compromise of efficiency and accuracy.

## V. THE PAULI HAMILTONIAN AND THE QUASIRELATIVISTIC METHOD: FROZEN CORES AND VARIATIONAL STABILITY

The Pauli Hamiltonian in general poses no problems for bound electrons if one uses it in a first order perturbation

theory, where the expectation value of the Pauli Hamiltonian with the nonrelativistic wave function is used. Snijders and Baerends<sup>24</sup> proposed a method for the calculation of relativistic effects in a perturbative procedure, where also first order effects in the change of the density are taken into account. In the numerical atomic calculations of Ref. 24 the correct boundary conditions were taken into account and no variational collapse can occur. This method, denoted first-order Pauli (PAULI FOPT), has been implemented and applied<sup>14,25</sup> in the molecular ADF program, i.e., using STO basis sets. The FOPT treatment implies diagonalization of the Pauli Hamiltonian in subspaces of (quasi-) degenerate levels.<sup>14</sup> It proved advantageous to apply this diagonalization in the full space of valence and virtual levels resulting from a frozen core calculation in the standard double-zeta or triple-zeta STO basis sets.<sup>26,27</sup> This so-called quasirelativistic (QR) procedure, which partially takes into account higher order effects, has become the standard procedure in relativistic ADF calculations. It has been observed empirically that variational collapse does not occur with the standard NR ADF basis sets, while the QR procedure still offers significant improvement over PAULI FOPT for heavy elements. In general, however, there are significant limitations on basis set choice in the QR Pauli method, as can be seen as follows.

First of all one may run into variational stability problems easily when including the core electrons in the SCF treatment (all-electron calculations). These problems with variational collapse are reduced (but not necessarily absent, see below) when the frozen core approximation is used. It is known that the PAULI FOPT approximation, using expectation values of the Pauli Hamiltonian for nonrelativistic orbitals, will improve the orbital energies. The QR Pauli method typically also uses nonrelativistic valence (and virtual) orbitals as basis. The nonrelativistic basis sets use one core orthogonalization function per core orbital to orthogonalize on the accurately calculated nonrelativistic core orbitals. The core orthogonalization functions are optimized to the core wiggles of the nonrelativistic valence orbitals. With good valence basis sets, the nonrelativistic solutions will be accurately described and a good performance of the PAULI FOPT as well as QR Pauli is expected. An example of this, calculations on the neutral Uranium atom, can be found in Refs. 26 and 28. If we calculate the U atom, using a standard basis, the so called ADF IV with  $5d$  frozen core, we obtain  $-1.30$  a.u. for the NR  $6s$  orbital energy, and  $-1.57$  a.u. and  $-1.75$  a.u. using FOPT and the QR method, respectively. This can be compared with the relativistic Dirac result of  $-1.72$  a.u., showing that the QR method improves upon the FOPT result considerably. The general observation was made in Ref. 27 that for elements up to  $Z=80$  PAULI FOPT

TABLE IV. SR ZORA (ESA) GGC optimized bond lengths  $r_e$  in angstroms for some diatomic systems, obtained from pointwise calculations and from analytical calculated geometry gradients.  $\Delta r_e$  is the difference in  $r_e$  between these methods.

	I <sub>2</sub>	Au <sub>2</sub>	Bi <sub>2</sub>	HI	AuH	TIH	IF	TIF	TII	PbO	PbTe
Pointwise	2.697	2.517	2.655	1.625	1.535	1.931	1.940	2.126	2.872	1.939	2.629
Analytical	2.699	2.518	2.656	1.625	1.537	1.929	1.941	2.127	2.874	1.939	2.629
$\Delta r_e$	0.002	0.001	0.001	0.000	0.002	-0.002	0.001	0.001	0.002	0.000	0.000

is accurate enough, while for heavier systems the QR method is needed.

However, the stability problems of the QR Pauli become apparent when we consider basis set variation. A first example is changing the core orthogonalization functions. Instead of using the STO's which are optimized to the core wiggles of the valence functions, we could use STO's optimized to the core orbitals, in the sense of having maximum overlap with the core orbital. With such core orthogonalization functions (still one per core orbital) we now get in the NR case  $-1.24$  a.u. for the  $6s$  orbital energy. This somewhat higher energy (than the  $-1.30$  a.u. quoted above) can be expected for a basis set which cannot describe the core wiggles of the valence orbitals as accurately as before. However, in the QR method we now already have problems related to variational collapse, the  $6s$  orbital energy in this case being  $-3.75$  a.u., which is far too low. The success of the QR method thus quite heavily depends on the choice of the core orthogonalization functions. A second example is to enlarge the standard ADF IV basis set with an extra STO in the basis which is corelike, for example a  $1s$ -type STO with  $\lambda = 40$ . In the NR calculation the  $6s$  energy is then still  $-1.30$  a.u., the difference being less than  $0.0001$  a.u. with respect to the calculation without this corelike function. Again this could be expected since the basis set was already quite optimal and a corelike function is certainly not able to improve much upon this. In the QR calculation, however, the  $6s$  orbital energy now becomes  $-485$  a.u., showing the drastic effect of variational collapse. In fact, it is possible to obtain any orbital energy by variation of the corelike basis functions.

In the QR method implemented in ADF, the variational collapse can thus be avoided by carefully choosing the basis set; the core orthogonalization functions should be optimized to core wiggles of nonrelativistic valence orbitals and the valence basis set should not contain too contracted functions and not be too extensive. The standard ADF frozen core basis sets fulfill all these requirements. Using these basis sets the QR method can then be a very useful (and cheap) method for estimating relativistic effects. However, it is not possible to investigate basis set effects, since enlarging the basis may yield unreliable results (see Sec. VI). The SR ZORA and ZORA method have been developed with the purpose to have efficient yet variationally stable relativistic methods that will allow one to obtain high accuracy by using extended basis sets.

## VI. RESULTS AND DISCUSSION

In this section we test our implementation of the calculation of the analytical energy gradients for SR ZORA on some small molecules using density functional theory. The usual (nonrelativistic) density functionals for the exchange-correlation energy are used; local density functionals (LDA) with gradient correction (GGC) terms added, namely the Becke correction for exchange<sup>20</sup> and the Perdew correction for correlation.<sup>21</sup>

In Ref. 29 results are given of all-electron density functional calculations of bond lengths for a number of diatomics. In Table IV these results, that were obtained by pointwise calculations of bond energies, are compared with the results that were obtained from calculations that use the analytical geometry gradients. In the present calculations the same large basis sets were used as in Ref. 29. These basis sets are triple- $\zeta$  in the core and quadruple- $\zeta$  in the valence with at least three polarization functions added. For the heavier atoms, these basis sets contain extra  $1s$  and  $2p$  STO functions, in order to describe the core orbitals accurately. The difference in the calculated bond lengths between the pointwise and analytical calculations is  $0.002$  Å at most. Small differences of this order were already reported in nonrelativistic calculations using the ADF program, see Ref. 16. Possible causes that were cited are related to features of the ADF methodology that limit the numerical precision, such as the density fitting procedure for obtaining the Coulomb potential and the numerical integration for Hamiltonian matrix elements. Since our present method only modifies the calculation of the kinetic energy gradient in comparison with the nonrelativistic case, a similar level of precision could be expected. Since the differences are so small we may conclude that the analytical calculation of the kinetic energy gradient in the ZORA ESA method, Eq. (20), gives results which are in very good agreement with those obtained with a point by point tracing of the energy.

Recently, geometry optimizations were performed by van Wüllen, Ref. 9, who uses the ZORA (MP) method. Results for some diatomics showed reasonable agreement with results that were obtained with the ZORA ESA method.<sup>6</sup> The remaining differences in the results of the two methods can be explained partly by the use of different basis sets, but we think that also a part of the deviations is due to the gauge dependence problems of the ZORA (MP) results, which were already explained at the end of Sec. III. Let us consider the example of AuH for a more quantitative analysis of these problems. In the ZORA (MP) method the kinetic energy of

the (deep) core orbitals on Au will depend on the actual distance between Au and H even if these (deep) core orbitals do not change shape. In this case the main effect comes from the part of the molecular model potential that is due to the H atom in the region of the Au nucleus, where the (deep) core orbitals have some value. In Ref. 9 the molecular model potential is constructed in such a way that distant atoms do not contribute, but in the AuH molecule the H atom is still so close to the Au atom, that a non-negligible contribution remains, which is larger if the atoms are closer. The resulting electrostatic shift in the molecular model potential in the region of the Au nucleus will lower the ZORA kinetic energy of the (deep) core orbitals. In the case of the exact solution of the hydrogen atom the sum of the nuclear potential and Coulomb potential of the electron density at 1.535 Å is approximately  $-0.11$  eV. A simple estimate of the gauge dependence error in the energy, see the end of Sec. III A, is this value of  $-0.11$  eV divided by  $2c^2$  and multiplied by the kinetic energy of the electrons of the gold atom ( $\approx 22\,000$  a.u.). We then obtain a value of  $-0.065$  eV for the gauge dependence error in the energy. If we do the same exercise at a AuH distance of 1.52 Å, we obtain a value of  $-0.069$  eV for this error. Since this gauge dependence error is larger at shorter distances it will also have an effect on the calculated bond length. The total error of this gauge dependence problem in the ZORA (MP) method can now be estimated for AuH as an increase in the bond energy in the order of 0.07 eV and a decrease in the bond length in the order of 0.01 Å. In Ref. 9 the ZORA (MP) results for AuH indeed showed a higher bond energy of 0.06 eV, and a shorter bond length of 0.02 Å, compared to the ZORA ESA results. Although this is close to our estimate of the error due to the gauge dependence problem in the ZORA (MP) method, one also has to take into account that different basis sets were used, which may be partly responsible for the differences. Also for other diatomics the gauge dependence problem will result in a too short bond length, and a too large bond energy. These errors will probably not be large, but they can be avoided completely if the ZORA ESA method is used, since this method was designed to solve the problem of gauge dependence, see also Ref. 6. On the basis of the presented analysis, a possible remedy for the gauge dependence problem in the ZORA (MP) method is to construct a model potential such that the electrostatic shift in the model potential due to an atom in the regions of other atoms is zero.

Next we test our implementation of the calculation of analytical gradients in the SR ZORA ESA method in a calculation of the structures of some polyatomic molecules, namely, the heavy transition metal compounds  $W(CO)_6$ ,  $Os(CO)_5$ , and  $Pt(CO)_4$ , since these have been studied extensively before.<sup>7,30–35,13</sup> In Table V results are given for the optimized metal–carbon distance and the first metal–carbonyl bond dissociation energy (FBDE).

We performed frozen core (fc) and all electron (ae) calculations, using different sizes of basis sets on the atoms. In the frozen core calculations the  $1s$  orbitals of carbon and oxygen were kept frozen. In the largest core ( $4f$ ) for the metal centers, the orbitals up to [Kr],  $4d, 4f$  were kept frozen, the subvalence  $5s, 5p$  shells being retained in the variational

space. The metal  $4f$  electrons were unfrozen in the ( $4d$ ) metal frozen core basis sets. For the metals new STO basis sets were created. The exponents of these STO's were fitted to numerical scalar relativistic ZORA orbitals. Basis set IV is double- $\zeta$  for  $5s, 5p$ , triple- $\zeta$  for the valence orbitals ( $5d, 6s$ ), and it has one  $6p$  function. In basis set V a  $5f$  polarization function is added. For C and O the basis sets IV and V that are used here in the SR ZORA calculation are the same as the standard ADF nonrelativistic basis sets. The QZD basis sets for carbon and oxygen are quadruple- $\zeta$  for the valence orbitals ( $2s, 2p$ ) plus one polarization function. These basis sets are given in Ref. 36, where also basis set superposition errors for these basis sets in the  $Cr(CO)_6$  and  $Mn_2(CO)_{10}$  complexes have been investigated. Comparing the SR ZORA calculations we conclude from Table V that the results of the frozen core calculations compare very well with our largest calculations, the all electron (ae) calculations. The different basis sets all give optimized bond lengths within 0.01 Å of each other, and FBDE's within 0.5 kcal/mol of each other. If for the metal the  $4d$  frozen core with basis set V is chosen, the results are in even better agreement with our largest calculations, the all electron calculations; within 0.2 kcal/mol for the FBDE and within 0.001 Å for the bond lengths.

We also performed pointwise calculations of the bond energy to obtain the optimal metal–carbon distance. For each compound these were determined in all-electron calculations and in one of the frozen core calculations. The optimized bond distances of these pointwise calculations were always within 0.002 Å of the analytically calculated distances. This again confirms that the analytical calculation of the kinetic energy gradient in the SR ZORA ESA method, according to Eq. (20), is in good agreement with the SR ZORA ESA method for the pointwise calculation of the bond energy.<sup>6</sup> In the pointwise calculation the CO distance was kept at the optimized bond length of the analytical calculation.

In Table V we also show the results of the optimized geometries obtained from quasirelativistic (QR) calculations, using the ADF program. Using the standard ADF basis sets IV for the atoms, very good results were obtained for the optimized bond lengths, if the results are compared with the SR ZORA ESA results (deviations less than 0.01 Å). FBDE's appear to be overestimated by 3–5 kcal/mol (10–30%). However, if we enlarge the basis set for carbon and oxygen to quadruple- $\zeta$  (QZD), variational collapse occurs, and especially the calculated FBDE is completely wrong. The origin of this variational collapse in the QR method of the Pauli Hamiltonian was explained in Sec. V. This example again shows the limitations on the use of this QR method if larger basis sets are used. This implies that the QR method only gives satisfactory results for moderate size basis sets, and one cannot obtain the basis set limit. Moreover, one cannot use an all electron basis set for the heavy atoms in order to test the frozen core approximation, since variational collapse would occur. On the other hand, as we have seen in Table V, in the SR ZORA ESA larger basis sets are not a problem, and one can study the convergence of the results to the basis set limit, and it is possible to test the frozen core approximation using all electron basis sets. For  $Pt(CO)_4$  we tested the remaining basis set error in the all-electron calcu-

TABLE V. Optimized metal–carbon bond lengths  $r(\text{M–CO})$  in angstroms and the first metal–carbonyl bond dissociation energies (FBDE) for  $\text{W}(\text{CO})_6$ ,  $\text{Os}(\text{CO})_5$ , and  $\text{Pt}(\text{CO})_4$ .

Method	M	C, O	$r(\text{M–CO})$	FBDE kcal/mol	
$\text{W}(\text{CO})_6$					
SR ZORA	(4f)IV	(1s)IV	2.070	44.6	
SR ZORA	(4f)IV	(1s)QZD	2.069	44.4	
SR ZORA	(4f)V	(1s)IV	2.068	44.6	
SR ZORA	(4d)V	(1s)IV	2.062	45.0	
SR ZORA	(ae)V	(ae)V	2.061	44.9	
QR	(4f)IV	(1s)IV	2.066	48.0	
QR	(4f)IV	(1s)QZD	2.049	64.0	
DFT DKH (Ref. 13)			2.063	46.9	
DFT DPT (Ref. 35)			2.060	46.1	
QR (Ref. 30)			2.049	43.7	
[CCSD(T)//MP2] RECP (Refs. 31, 32)			2.060	48.0	
Experiment (Refs. 37, 38)			2.058	46±2	
$\text{Os}(\text{CO})_5$					
			axial	equatorial	
SR ZORA	(4f)IV	(1s)IV	1.974	1.959	37.5
SR ZORA	(4f)IV	(1s)QZD	1.973	1.958	37.3
SR ZORA	(4f)V	(1s)IV	1.970	1.955	37.6
SR ZORA	(4d)V	(1s)IV	1.967	1.951	37.7
SR ZORA	(ae)V	(ae)V	1.966	1.950	37.5
QR	(4f)IV	(1s)IV	1.968	1.949	42.9
QR	(4f)IV	(1s)QZD	2.017	1.757	191.5
DFT DPT (Ref. 35)			1.964	1.949	37.5
QR (Ref. 30)			2.000	1.975	34.7
[CCSD(T)//MP2] RECP (Refs. 33, 34)			1.963	1.945	42.9
Experiment (Refs. 39, 40)			1.990	1.943	(30.6)
$\text{Pt}(\text{CO})_4$					
SR ZORA	(4f)IV	(1s)IV	1.975	14.8	
SR ZORA	(4f)IV	(1s)QZD	1.976	14.5	
SR ZORA	(4f)V	(1s)IV	1.973	14.7	
SR ZORA	(4d)V	(1s)IV	1.967	14.7	
SR ZORA	(ae)V	(ae)V	1.967	14.5	
QR	(4f)IV	(1s)IV	1.959	19.0	
QR	(4f)IV	(1s)QZD	1.874	8.2	
DFT DPT (Ref. 35)			1.963	12.4	
QR (Ref. 30)			2.012	15.7	
[CCSD(T)//MP2] RECP (Refs. 33, 34)			1.966	12.1	
Experiment			...	...	

lations, using basis sets of the size that were already used in the calculation of the bond lengths of the diatomics. Using these large basis sets the optimized platinum–carbon bond length is 1.964 Å and the FBDE is 14.3 kcal/mol. These results are very close to those obtained with the all electron basis set V; they only differ 0.003 Å in the optimized bond length and 0.2 kcal/mol in the calculated FBDE.

In Table V our results are compared with recent results that were obtained using the leading order of the relativistic direct perturbation theory (DPT),<sup>35</sup> and for  $\text{W}(\text{CO})_6$  with results of the Douglas–Kroll–Hess (DKH) (Ref. 13) method, using the same density functional as in the present work. The leading order of the relativistic DPT without spin–orbit coupling means that only the well known mass–velocity term and Darwin term of the Pauli Hamiltonian were included. The results for the bond lengths and FBDE's are in very satisfactory agreement with our results. The bond lengths agree within 0.004 Å, while the FBDE exhibits a largest deviation of 2.1 kcal/mol (for  $\text{Pt}(\text{CO})_4$ ). It should be noted that different basis sets were used and that the ZORA

method includes higher order relativistic effects than the Pauli Hamiltonian. Comparison to the previous QR Pauli results of Li *et al.*<sup>30</sup> shows good agreement in general, with largest differences with the present (ae) SR ZORA results of 0.05 Å for the Pt–C distance and 2.8 kcal/mol for the Os–CO FBDE. The results for  $\text{W}(\text{CO})_6$  of the scalar relativistic DKH method, which also contains higher order relativistic effects, are in close agreement with the SR ZORA results.

In Table V our results are also compared with *ab initio* results at the [CCSD(T)//MP2] level of theory using relativistic effective core potentials (RECP).<sup>31–34</sup> Again these results agree well with our results, with largest differences of 0.005 Å for the equatorial Os–C distance and 5.4 kcal/mol for the Os–CO FBDE.

## VII. CONCLUSION

Expressions have been derived for the evaluation of energy gradients in the ZORA ESA method and were imple-

mented in the ADF program. The approximations made in the derivation were validated by the very close agreement in the bond lengths that were obtained by pointwise calculation of bond energies with the bond lengths that were obtained from calculations that use the analytical geometry gradients. It was shown that these analytical expressions are easier to evaluate than the expressions following from the recently developed ZORA (MP) method, and that they do not have the gauge dependence problem that still exists in the ZORA (MP) method.

In contrast with a quasirelativistic (QR) method based on the Pauli Hamiltonian previously implemented in the ADF program, in the SR ZORA ESA method it is possible to study the convergence of the optimized bond lengths and bond energies with respect to the basis set limit, and one can test the frozen core approximation using all electron basis sets. It was explained why and when in the QR method variational collapse occurs.

The structures and first metal–carbonyl bond dissociation energies for the transition metal complexes  $W(CO)_6$ ,  $Os(CO)_5$ , and  $Pt(CO)_4$  were calculated with the SR ZORA ESA method and smooth convergence of the results with respect to the size of basis set were obtained. Comparisons have been made to results of previous *ab initio* calculations at the [CCSD(T)//MP2] level of theory using relativistic effective core potentials, with QR Pauli DFT calculations, with DFT density functional calculations, and with Douglas–Kroll–Hess density functional calculations. No major discrepancies between these calculations have been found, although occasionally differences of several hundredths of an Å and several kcal/mol were observed.

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