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An *ab initio* two-component relativistic method including spin–orbit coupling using the regular approximation

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In this paper we present the implementation of the two-component scaled zeroth-order regular approximation (ZORA) method in the molecular electronic structure package GAMESS-UK. It is the first application of this method, which was earlier investigated in the context of density functional theory, in molecular *ab initio* basis set calculations. The performance of the method is tested in atomic calculations, which we can compare with numerical results, on xenon and radon and in molecular calculations on the molecules AgH, HI, I_2, AuH, TlH, and Bi_2. In calculations on the I_2 molecule we investigated the effect of the different approaches regarding the internal Coulomb matrix used in the ZORA method. For the remaining molecules we computed harmonic frequencies and bond lengths. It is shown that the scaled ZORA approach is a cost-effective alternative to the Dirac–Fock method. © *2000 American Institute of Physics*. [S0021-9606(00)32034-7]

I. INTRODUCTION

The inclusion of relativistic effects is essential in the quantum chemical description of compounds containing one or more heavier elements, see, e.g., Ref. 1. Highly accurate, but unfortunately extremely costly, calculations can be performed using the full theory of quantum electrodynamics. Due to the computational requirements, these calculations can only be performed on small atomic systems. To be able to treat systems of chemical interest it is therefore necessary to make approximations.

An accurate method is based on the solution of the four-component Dirac–Fock equations, the relativistic analog of Hartree–Fock. This method is still very costly mainly because of the use of large basis sets needed for a proper description of the small component. An attractive alternative is to transform the four-component Dirac equation to a two-, or even one-, component formalism. The ZORA (zeroth-order regular approximation) or CPD method, originally developed by Chang, Pellisier, and Durand and by Heully *et al.*[2,3] and later generalized to molecular density functional theory by van Lenthe, Baerends, and Snijders[4,5] and in its scalar form to *ab initio* methods by the present authors,[6,7] performs such a transformation. A calculation based on the ZORA method can therefore, in principle, be performed using only a large component basis, thereby circumventing the use of kinetically balanced basis sets. Since the ZORA orbitals resemble the Dirac large components spinors,[8] we can make use of basis sets optimized originally for Dirac–Fock calculations, see, e.g., Ref. 15.

In the present paper we present the first implementation and applications of the two-component ZORA Hamiltonian within an *ab initio* basis set framework. Unlike the earlier described scalar ZORA Hamiltonian,[7] this Hamiltonian includes spin–orbit coupling. We give a short review of the theory followed by details of the implementation of the method in the GAMESS-UK package.[9] Within this implementation there is room for several approaches regarding the so-called internal Coulomb matrix. An explanation of this concept and the different approximations used will be given. These approximations are tested in calculations on the I_2 molecule.

We test our implementation by calculations on the xenon and radon atoms. These atomic calculations are compared with numerical ZORA calculations using our ZORA implementation in the GRASP2 program.[10]

In molecular calculations on the diatomics I_2, HI, AgH, AuH, TlH, and Bi_2 we investigate the performance of the ZORA Hamiltonian. The quality of the wave functions is asserted by comparison of orbital energies (I_2) with four-component Dirac–Fock results, obtained using the MOLFDIR program package.[11] The calculations on the equilibrium geometries and harmonic frequencies of the molecules HI, AgH, AuH, TlH and Bi_2 are used to test the validity of the one-center approximation to the internal Coulomb matrix. Furthermore the results are compared with experiment and full Dirac–Fock results obtained with the DIRAC program.[12] The comparison with scalar ZORA calculations unveils the effect of the inclusion of spin–orbit coupling in the self-consistent field (SCF) procedure.

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II. THEORY

Using an expansion in $E/(2c^2-V)$ on the Foldy–Wouthuysen transformed Dirac–Fock equation one can derive the *ab initio* ZORA and scaled ZORA equations.[6] The equations, which still contain the large and small components of the Dirac spinor, read

$$F^{\mathrm{ZORA}}\psi_i=\epsilon_i^{\mathrm{ZORA}}\psi_i, \quad \frac{1}{\mathcal{S}}F^{\mathrm{ZORA}}\psi_i=\epsilon_{\mathrm{scaled},i}^{\mathrm{ZORA}}\psi_i, \tag{1}$$

where ψ_i is the two-component ZORA orbital. The ZORA Fock operator is given by

$$F^{\mathrm{ZORA}}=(c\boldsymbol{\sigma}\cdot\mathbf{p}-K_{\phi\chi})\frac{1}{(2c^2-V_c^{\phi\chi}+K_{\chi\chi})}(c\boldsymbol{\sigma}\cdot\mathbf{p}-K_{\chi\phi}) + V_c^{\phi\chi}-K_{\phi\phi} \tag{2}$$

and the scaling factor by

$$\mathcal{S}=1+\langle\psi_i|(c\boldsymbol{\sigma}\cdot\mathbf{p}-K_{\phi\chi}) \times\frac{1}{(2c^2-V_c^{\phi\chi}+K_{\chi\chi})^2}(c\boldsymbol{\sigma}\cdot\mathbf{p}-K_{\chi\phi})|\psi_i\rangle. \tag{3}$$

We use the abbreviation

$$V_c^{\phi\chi}=V_{\mathrm{nuc}}+J_{\phi\phi}+J_{\chi\chi}. \tag{4}$$

The large and small components of the original Dirac spinor are denoted by ϕ_i and χ_i. The relation between ψ_i, ϕ_i, and χ_i is determinated by the Foldy–Wouthuysen transformation[6] and has become energy independent by the use of the expansion in $E/(2c^2-V)$. J and K are the Coulomb and exchange operators, c is the speed of light, $\boldsymbol{\sigma}$ are the Pauli matrices. Equations (2) and (3) differ from the local density form derived earlier[4,5] by the presence of the exchange operators $K_{\phi\chi}$ and $K_{\chi\phi}$ coupling the large and small components. Another difference can be found in the density used in the different exchange potentials in the denominator of the ZORA kinetic energy term. In the present formulation based on Dirac–Fock, we have an exchange potential $K_{\chi\chi}$ only due to the small–small density

$$\rho^{\mathrm{SS}}(\mathbf{r},\mathbf{r}')=\sum_{i\mathrm{occ}}\chi_i^\dagger(\mathbf{r})\chi_i(\mathbf{r}'), \tag{5}$$

whereas the exchange–correlation potential used in the density functional theory (DFT) case contains the total density

$$\rho(\mathbf{r})=\sum_{i\mathrm{occ}}\phi_i^\dagger(\mathbf{r})\phi_i(\mathbf{r})+\chi_i^\dagger(\mathbf{r})\chi_i(\mathbf{r}). \tag{6}$$

Furthermore, the remaining exchange term in the *ab initio* Fock operator contains the large component density. The density functional formulation again uses an exchange–correlation potential containing the total density.

At this point the density is still calculated from the large and small component spinors obtained from the backtransformed ZORA orbitals. An easier and more practical SCF procedure is obtained when we lose all dependence on the small components.[6] In order to achieve this we make use of an approximate density derived directly from the ZORA orbitals

$$\rho(\mathbf{r},\mathbf{r}')=\sum_{i\mathrm{occ}}\psi_i^\dagger(\mathbf{r})\psi_i(\mathbf{r}'). \tag{7}$$

It implies

$$J_{\phi\phi}+J_{\chi\chi}\approx J_{\psi\psi}. \tag{8}$$

In the same spirit we assume

$$K_{\phi\phi}\approx K_{\psi\psi}, \quad K_{\phi\chi},K_{\chi\phi}\approx 0. \tag{9}$$

This leads to the removal of the off-diagonal and small component Coulomb and exchange operators. The resulting ZORA Fock operator is given by

$$F^{\mathrm{ZORA}}=\boldsymbol{\sigma}\cdot\mathbf{p}\frac{c^2}{2c^2-V_c^\psi}\boldsymbol{\sigma}\cdot\mathbf{p}+V_c^\psi-K_{\psi\psi} \tag{10}$$

with

$$V_c^\psi=V_{\mathrm{nuc}}+J_{\psi\psi} \tag{11}$$

and the scaling factor

$$S=1+\langle\psi_i|(\boldsymbol{\sigma}\cdot\mathbf{p})\frac{c^2}{(2c^2-V_c^\psi)^2}(\boldsymbol{\sigma}\cdot\mathbf{p})|\psi_i\rangle. \tag{12}$$

We can now perform two-component ZORA calculations using only a large component basis set.

III. IMPLEMENTATION

The two-component ZORA method is implemented in a separate module in the GAMESS-UK package[9] that allows only SCF calculations. The difference from the previously presented scalar ZORA scheme is that the ZORA Fock operator (10) contains the spin operators $\boldsymbol{\sigma}$. Hence, the orbitals have to be expanded in a set of spin orbitals $\{\phi\zeta\}$, with ϕ the spatial and ζ the spin part (either α or β). The ith ZORA orbital can be written as

$$\psi_i(\mathbf{r},s)=\sum_\mu c_{\mu,i}^\alpha\phi_\mu(\mathbf{r})\alpha(s)+c_{\mu,i}^\beta\phi_\mu(\mathbf{r})\beta(s), \tag{13}$$

where $\mathbf{r}$ denotes the spatial coordinate and s the spin coordinate. Note that the coefficients $c_{\mu,i}^\alpha$ and $c_{\mu,i}^\beta$ can be, and in general are, complex. The total density matrix can be written as

$$\begin{pmatrix} p^{\alpha\alpha} & p^{\alpha\beta} \\ p^{\beta\alpha} & p^{\beta\beta} \end{pmatrix} \tag{14}$$

with

$$p_{\mu\nu}^{\zeta\eta}=\sum_{i\mathrm{occ}}c_{\mu,i}^{\zeta*}c_{\nu,i}^\eta, \quad \zeta,\eta=\alpha \text{ or } \beta. \tag{15}$$

These matrices have the properties

$$p^{\alpha\alpha}=(p^{\alpha\alpha})^\dagger, \quad p^{\beta\beta}=(p^{\beta\beta})^\dagger, \quad p^{\beta\alpha}=(p^{\alpha\beta})^\dagger \tag{16}$$

and in the closed shell case we have the additional relation $p^{\alpha\alpha}=(p^{\beta\beta})^\dagger$. The real parts of $p^{\alpha\alpha}$ and $p^{\beta\beta}$ are symmetric, whereas the imaginary parts of $p^{\alpha\alpha}$ and $p^{\beta\beta}$ and the real and imaginary parts of $p^{\beta\alpha}$ and $p^{\alpha\beta}$ are antisymmetric. The total density can be written as

$$\rho(\mathbf{r})=\sum_{i}^{\mathrm{occ}}\int_{s}|\psi_i(\mathbf{r},s)|^2\,ds$$

$$=\sum_{\mu,\nu}(p_{\mu\nu}^{\alpha\alpha}+p_{\mu\nu}^{\beta\beta})\phi_\mu(\mathbf{r})\phi_\nu(\mathbf{r}). \tag{17}$$

The properties ensure the fact that the total density, as given in Eq. (17), remains real in spite of the complex density matrices, even in an open shell case where $(p^{\alpha\alpha}+p^{\beta\beta})_{\mu\nu}$ can have imaginary elements. Moreover we see that the two-electron part of the Fock matrix is Hermitian. The total two-electron Fock matrix can be written as

$$\begin{pmatrix} J^{\alpha\alpha}-K^{\alpha\alpha} & K^{\alpha\beta} \\ K^{\beta\alpha} & J^{\beta\beta}-K^{\beta\beta}\end{pmatrix} \tag{18}$$

with

$$J_{\mu\nu}^{\alpha\alpha}=J_{\mu\nu}^{\beta\beta}=\sum_{\kappa,\lambda}(p_{\kappa\lambda}^{\alpha\alpha}+p_{\kappa\lambda}^{\beta\beta})(\phi_\mu\phi_\nu|\phi_\lambda\phi_\kappa) \tag{19}$$

and

$$K_{\mu\nu}^{\zeta\eta}=\sum_{\kappa,\lambda}p_{\kappa\lambda}^{\zeta\eta}(\phi_\mu\phi_\kappa|\phi_\lambda\phi_\nu), \tag{20}$$

where ζ and η are either α or β. The two-electron matrices originating from the symmetric (parts of the) density matrices can be constructed using the, already available, unrestricted Hartree–Fock matrix builders. The antisymmetric (parts of the) density matrix, however, required the development of new code.

The one-electron part of the Fock matrix requires the evaluation of the matrix elements of T^{ZORA},

$$T_{\mu\nu}^{\mathrm{ZORA}}=\frac{1}{2}\langle\phi_\mu\zeta_\mu|\boldsymbol{\sigma}\cdot\mathbf{p}\frac{1}{1-\dfrac{V_c}{2c^2}}\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\zeta_\nu\rangle. \tag{21}$$

These matrix elements can be calculated most easily by insertion of resolutions of identity[13]. Furthermore we split off the nonrelativistic kinetic energy. We write

$$\begin{aligned}T_{\mu\nu}^{\mathrm{ZORA}}=&\frac{1}{2}\langle\phi_\mu\zeta_\mu|p^2|\phi_\nu\zeta_\nu\rangle-\frac{1}{2}\sum_{\lambda}\langle\phi_\mu\zeta_\mu|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\lambda\zeta_\lambda\rangle\\&\times S_\phi^{-1}\langle\phi_\lambda\zeta_\lambda|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\zeta_\nu\rangle\\&+\frac{1}{2}\sum_{\lambda,\kappa}\langle\phi_\mu\zeta_\mu|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\lambda\zeta_\lambda\rangle S_\phi^{-1}\\&\times\langle\phi_\lambda\zeta_\lambda|1-\frac{V_c}{2c^2}|\phi_\kappa\zeta_\kappa\rangle^{-1}\\&\times S_\phi^{-1}\langle\phi_\kappa\zeta_\kappa|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\zeta_\nu\rangle,\end{aligned} \tag{22}$$

where S_ϕ^{-1} is the inverted metric in the nonorthogonal basis. In the last term of Eq. (22) we have used an inner projection, replacing the matrix of an inverse operator by the matrix inverse of the operator.

This procedure has two advantages. First, we now need a basis set in the resolution of the identity that is complete in the range of $V_c/2c^2$. In the region where $V_c/2c^2$ is negligible the terms arising from the incompleteness of the resolution cancel in the second and third terms of Eq. (22). T^{ZORA} then reduces to $p^2/2$, the nonrelativistic kinetic energy operator. If we would have inserted the resolutions directly into Eq. (21) we would only have had a reliable representation of the matrix elements if the resolutions were complete in the range of $\boldsymbol{\sigma}\cdot\mathbf{p}$ and $1/(1-V_c/2c^2)$. This is a far more severe requirement.

Second, the splitting off of the nonrelativistic kinetic energy ensures us of having the correct answer in the nonrelativistic limit ($c\to\infty$). Direct use of the resolutions in Eq. (21) leads, in this limit, to the approximation

$$T_{\mu\nu}=\frac{1}{2}\sum_{\lambda}\langle\phi_\mu\zeta_\mu|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\lambda\zeta_\lambda\rangle S_\phi^{-1}\langle\phi_\lambda\zeta_\lambda|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\zeta_\nu\rangle \tag{23}$$

of the nonrelativistic kinetic energy, again requiring the resolution to be complete in the range of $\boldsymbol{\sigma}\cdot\mathbf{p}$. In Eq. (22) the last two terms cancel in the nonrelativistic limit since $1-V_c/2c^2$ reduces to 1.

We now show that we can rewrite all terms in the ZORA kinetic energy (22) in terms of already available gradient integrals. To this end we realize that the Gaussian basis set functions used depend on the difference of the electronic ($\mathbf{r}$) and nuclear ($\mathbf{r}_N$) coordinates only: $\phi_\mu(\mathbf{r}-\mathbf{r}_N)$. So

$$\begin{aligned}\langle\phi_\mu\alpha|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\alpha\rangle&=+i\langle\phi_\mu|\frac{\partial}{\partial Z_N}|\phi_\nu\rangle,\\\langle\phi_\mu\beta|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\beta\rangle&=-i\langle\phi_\mu|\frac{\partial}{\partial Z_N}|\phi_\nu\rangle,\end{aligned} \tag{24}$$

and

$$\langle\phi_\mu\alpha|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\beta\rangle=i\langle\phi_\mu|\frac{\partial}{\partial X_N}-i\frac{\partial}{\partial Y_N}|\phi_\nu\rangle. \tag{25}$$

Where we used the standard representation of the spin operators, the Pauli matrices

$$\sigma_x=\begin{pmatrix}0&1\\1&0\end{pmatrix},\quad\sigma_y=\begin{pmatrix}0&-i\\i&0\end{pmatrix},\quad\sigma_z=\begin{pmatrix}1&0\\0&-1\end{pmatrix}. \tag{26}$$

The spin functions are then represented by $\alpha=\binom{1}{0}$ and $\beta=\binom{0}{1}$. Consider, e.g., the $\alpha\alpha$ part of the second term of Eq. (22). Using the relations in Eqs. (24) and (25) we write

$$\begin{aligned}\sum_{\lambda}\sum_{\zeta=\alpha,\beta}&\langle\phi_\mu\alpha|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\lambda\zeta\rangle S_\phi^{-1}\langle\phi_\lambda\zeta|\boldsymbol{\sigma}\cdot\mathbf{p}|\phi_\nu\alpha\rangle\\&=D_z\cdot D_z+D_x\cdot D_x+D_y\cdot D_y+i(D_x\cdot D_y-D_y\cdot D_x),\end{aligned} \tag{27}$$

where D_i denotes the derivative of the overlap matrix with respect to nuclear coordinate i_N,

$$(D_i)_{\mu\nu}=\langle\phi_\mu|\frac{\partial}{\partial_{i_N}}|\phi_\nu\rangle,\quad i_N=X_N,Y_N,Z_N \tag{28}$$

and the dot is used to represent a standard matrix multiplication in a nonorthogonal basis

$$(A\cdot B)_{\mu\nu}=\sum_{\kappa\kappa'}A_{\mu\kappa}(S_\phi)_{\kappa\kappa'}^{-1}B_{\kappa'\nu}. \tag{29}$$

The $\alpha\beta$, $\beta\alpha$, and $\beta\beta$ contributions can be rewritten in the same way. The last term of Eq. (22) contains no extra difficulties since $\langle \phi_\lambda \zeta_\lambda | 1-(V_c/2c^2) | \phi_\kappa \zeta_\kappa \rangle$ is diagonal in spin (so $\zeta_\lambda = \zeta_\kappa$). The real part, $D_z \cdot D_z + D_x \cdot D_x + D_y \cdot D_y$, is also present in our implementation of the scalar ZORA method.

As noted earlier,[7] it is convenient to use two different basis sets in our calculations. The first one, the external basis, is the one used in the electronic structure calculation. The latter, the internal basis, is the one used in the resolution of the identity. There are two aspects in the construction of the internal basis.

(1) The $\langle \phi | \mathbf{p} | \chi \rangle \langle \chi | (\cdots)$ products of integrals should be correctly represented. Consider a matrix element $\langle s | \mathbf{p} | p \rangle$, where s and p denote an s- and p-type Gaussian basis function. The momentum operator working on a high exponent $\langle s |$ produces a $\langle p |$ with the same exponent. This high exponent p-type Gaussian is, in general, not present in our external basis set. The internal basis, however, should contain this function. Generalizing this argument to p-, d-, and f-type functions we see that the matrix elements are represented exactly if we define our internal basis as $\{\chi\} \subset \mathbf{p} \cdot \{\phi\}$.

(2) The Coulomb matrix $V_C^{\psi} = V_{\text{nuc}} + J_{\psi\psi}$ appearing in the inverse operator needs to be evaluated in the internal basis. This is generally done by projecting the external density matrix onto the internal basis and building the Coulomb potential from the resulting density. This projection is exact if the internal basis contains the external basis. Hence the condition: $\{\chi\} \subset \{\phi\}$ ensures an exact projection.

In practice we have chosen to construct the internal basis by copying all functions from the external basis onto the internal basis, thereby fulfilling the second condition completely. The internal basis is successively augmented with p-type functions with exponents of external s- functions higher than the highest external p-type functions; with d-type functions with exponents of external p-functions higher than the highest external d-type functions; and so on. This means that we approximate the first condition. The resulting internal basis (size N_{int}) is usually considerably bigger than the external basis (size N_{ext}).

The evaluation of the Coulomb matrix in the internal basis is done using a direct algorithm. The screening of integrals ensures the fact that we only compute integrals that are contracted with a nonzero element of the density matrix. Consequently, integrals of the type $(\chi\chi|\chi\chi)$ are avoided and the calculation of the internal Coulomb matrix is an operation of order $N_{\text{ext}}^2 N_{\text{int}}^2$ instead of N_{int}^4.

To be able to reduce the computational work even further we have implemented several possibilities for the construction of the internal Coulomb matrix.

(1) Project the external density matrix onto the internal basis and build the full or one-center Coulomb matrix. The latter is of course an approximation of the first, but, since $V_c/2c^2$ is only large near the nuclei, we expect that this extra approximation does not result in a serious loss of accuracy. The effect of the one-center approximation has been investigated and will be commented on in Sec. V. This approximation has been made to reduce the computational cost of the evaluation of the two-electron Coulomb matrix in the internal basis. Note that it is also necessary to build the one-electron part (V_{nuc}) with only intra-atomic parts.

(2) Use the density of the atomic startup for evaluation of the Coulomb matrix in the ZORA corrections and keep the ZORA corrections constant during the remainder of the SCF procedure.

IV. BASIS SETS

In the calculations on the xenon atom we have used two different basis sets. The first one, which we will call ''adjusted Huzinaga,'' was originally developed for nonrelativistic calculations[14] and was augmented with extra high exponent s- and p-type functions and with diffuse d- and f-type functions to account for the relativistic contraction and expansion of the corresponding orbitals. The basis set is used uncontracted. The second basis set is taken from Dyall[15] and is the large component basis of a basis originally developed for Dirac–Fock calculations. It is again used uncontracted. In the case of the radon atom we followed the same recipe as for the xenon ''adjusted Huzinaga'' set. In the corresponding Dirac–Fock calculation the small component functions were generated by kinetic balance.

In the case of the I_2 molecule we used a basis from Poirier, Kari, and Csizmedia[16] again augmented with extra functions and used uncontracted.

The calculations on the HI molecule were performed with a Dyall set[15] on I. The basis sets used on the silver, gold, thallium, and bismuth atoms are again based on nonrelativistic basis sets taken from Huzinaga and adjusted to incorporate relativistic effects. In all cases we used a SV 3-21G set on hydrogen.[17]

The adjusted Huzinaga and Poirier sets are available upon request. All molecular calculations have been performed using spherical harmonic functions. The atomic calculations are performed using a Cartesian basis.

V. RESULTS

A. Atomic calculations

Table I lists the orbital energies for the xenon atom from numerical as well as basis set Dirac–Fock and scaled ZORA calculations. The basis set results are obtained with the adjusted Huzinaga set and the larger basis set from Dyall.

Looking at the numerical results we see that, except for the deep core region, the scaled ZORA method reproduces the Dirac–Fock results closely. The error ranges from 1.73 hartree for the $1s$ to 0.0001 hartree for the $5p_{3/2}$.

The basis set error can be compared for the adjusted Huzinaga and Dyall basis sets. For both sets it is seen that the basis set error made by scaled ZORA is of the same order in magnitude as the basis set error in the Dirac–Fock calculation in the same set. Sometimes, however, the error in the scaled ZORA results is slightly larger. This is probably due to the incompleteness of the internal basis. Of course, the absolute value of the basis set error, for both methods, is smaller in the larger basis set from Dyall.

The relativistic effect in the orbital energies of the xenon atom is 50 hartree for the $1s$ and decreases to 0.06 hartree, which is still significant, for the $5s$ orbital. The spin–orbit splitting in the $5p$ shell is still 0.05 hartree.

TABLE I. Orbital energies for the xenon atom obtained with the Dirac–Fock and scaled ZORA methods.

	Dirac–Fock numeric	ZORA numeric	Dirac–Fock Huzinaga[a]	ZORA Huzinaga[a]	Dirac–Fock Dyall[b]	ZORA Dyall[b]
$1s$	−1277.3687	−1275.6352	−1276.2021	−1274.8530	−1277.2511	−1275.5423
$2s$	−202.4784	−202.2698	−202.3546	−202.2127	−202.4603	−202.2547
$2p_{1/2}$	−189.6793	−189.6160	−189.6442	−189.4510	−189.6729	−189.5154
$2p_{3/2}$	−177.7038	−177.5994	−177.7118	−177.6218	−177.7003	−177.6275
$3s$	−43.0131	−42.9738	−42.9836	−42.9724	−43.0057	−42.9673
$3p_{1/2}$	−37.6598	−37.6513	−37.6609	−37.6068	−37.6549	−37.6120
$3p_{3/2}$	−35.3251	−35.3078	−35.3345	−35.3215	−35.3208	−35.3156
$3d_{3/2}$	−26.0232	−26.0232	−26.0162	−26.0045	−26.0181	−26.0117
$3d_{5/2}$	−25.5369	−25.5311	−25.5382	−25.5313	−25.5323	−25.5308
$4s$	−8.4305	−8.4232	−8.4254	−8.4246	−8.4255	−8.4185
$4p_{1/2}$	−6.4525	−6.4520	−6.4525	−6.4340	−6.4479	−6.4315
$4p_{3/2}$	−5.9827	−5.9804	−5.9848	−5.9870	−5.9785	−5.9823
$4d_{3/2}$	−2.7113	−2.7125	−2.7095	−2.7066	−2.7069	−2.7046
$4d_{5/2}$	−2.6337	−2.6339	−2.6337	−2.6350	−2.6294	−2.6316
$5s$	−1.0102	−1.0094	−1.0092	−1.0098	−1.0070	−1.0061
$5p_{1/2}$	−0.4926	−0.4927	−0.4924	−0.4871	−0.4888	−0.4840
$5p_{3/2}$	−0.4398	−0.4397	−0.4398	−0.4417	−0.4367	−0.4385

[a]Modified, based on Ref. 14.
[b]Reference 15.

The method has also been tested on the heavier radon atom, Table II. The relativistic effects in this atom are even larger, ranging from 414 hartree on the $1s$ orbital to 0.2 hartree on the $6s$. The spin–orbit splitting is as large as 101 hartree for the $2p$ shell and decreases to 0.16 hartree in the valence shell.

The numerical scaled ZORA results deviate significantly from the numerical Dirac–Fock results in the deep core region. The errors are 9.1 and 1.3 hartree for the $1s$ and $2s$ orbitals, respectively. However, even here the error is small compared to the relativistic effect. The agreement in the (sub) valence shells is very good.

Comparing the basis set results for Dirac–Fock and scaled ZORA, obtained in the adjusted Huzinaga set, with the numerical results, we see that the basis set errors are again of the same order in magnitude. The basis set errors are always significantly smaller that the size of the relativistic effect.

TABLE II. Orbital energies for the radon atom obtained with the Dirac–Fock, scaled ZORA, and nonrelativistic method.

	Dirac–Fock numeric	ZORA numeric	Dirac–Fock Huzinaga[a]	ZORA Huzinaga[a]	Nonrel. numeric	
$1s$	−3644.8056	−3635.6847	−3635.2927	−3627.6551	−3230.3128	$1s$
$2s$	−669.3867	−668.0729	−665.0317	−666.0655	−556.9131	$2s$
$2p_{1/2}$	−642.3553	−641.7975	−641.1660	−639.2556	−536.6770	$2p$
$2p_{3/2}$	−541.0813	−540.5567	−541.7030	−541.4071		
$3s$	−166.9675	−166.6788	−165.2106	−165.9139	−138.4219	$3s$
$3p_{1/2}$	−154.9012	−154.7955	−154.6073	−154.1382	−128.6716	$3p$
$3p_{3/2}$	−131.7246	−131.6164	−131.8994	−131.9312		
$3d_{3/2}$	−112.5611	−112.5389	−112.3169	−112.1751	−110.7013	$3d$
$3d_{5/2}$	−107.7535	−107.7045	−107.7484	−107.6409		
$4s$	−41.3487	−41.2782	−40.8703	−41.0651	−33.9207	$4s$
$4p_{1/2}$	−36.0209	−36.0002	−35.9615	−35.8068	−29.4912	$4p$
$4p_{3/2}$	−30.1186	−30.0962	−30.1860	−30.2115		
$4d_{3/2}$	−21.5464	−21.5465	−21.4956	−21.4501	−21.3313	$4d$
$4d_{5/2}$	−20.4371	−20.4305	−20.4580	−20.4345		
$4f_{5/2}$	−9.1927	−9.1990	−9.2241	−9.2120	−10.1076	$4f$
$4f_{7/2}$	−8.9270	−8.9293	−8.9644	−8.9575		
$5s$	−8.4168	−8.4025	−8.3145	−8.3572	−6.9058	$5s$
$5p_{1/2}$	−6.4090	−6.4066	−6.4021	−6.3465	−5.2252	$5p$
$5p_{3/2}$	−5.1752	−5.1724	−5.1949	−5.2058		
$5d_{3/2}$	−2.1892	−2.1910	−2.1844	−2.1712	−2.3263	$5d$
$5d_{5/2}$	−2.0161	−2.0168	−2.0232	−2.0194		
$6s$	−1.0727	−1.0707	−1.0559	−1.0620	−0.8740	$6s$
$6p_{1/2}$	−0.5403	−0.5404	−0.5398	−0.5216	−0.4280	$6p$
$6p_{3/2}$	−0.3839	−0.3839	−0.3866	−0.3896		

[a]Modified, based on Ref. 14.

TABLE III. Orbital energies of selected orbitals of I_2 at 5.0 bohr, obtained with the scaled ZORA method, using different Coulomb options and the Dirac–Fock method.

	Dirac–Fock	ZORA full	ZORA one center	ZORA atomic start
1σ	−1225.9171	−1224.3790	−1224.3786	−1224.3839
2σ	−193.0169	−192.8347	−192.8346	−192.8355
	−180.4957	−180.2990	−18.2989	−180.2998
2π	−169.5547	−169.4885	−169.4884	−169.4886
	−169.5538	−169.4874	−169.4874	−169.4876
4σ	−7.7508	−7.7548	−7.7458	−7.7458
	−5.8583	−5.8416	−5.8416	−5.8416
4π	−5.4490	−5.4541	−5.4541	−5.4541
	−5.4384	−5.4428	−5.4428	−5.4428
	−2.3304	−2.3298	−2.3298	−2.3298
	−2.3134	−3.3128	−2.3128	−2.3128
4δ	−2.2655	−2.2686	−2.2686	−2.2686
	−2.2566	−2.2595	−2.2595	−2.2595
	−2.2427	−2.2454	−2.2454	−2.2454
5σ	−0.9749	−0.9751	−0.9751	−0.9751
$5\sigma^*$	−0.8421	−0.8421	−0.8421	−0.8421
5σ	−0.4678	−0.4645	−0.4645	−0.4645
$5\pi_{1/2}$	−0.4589	−0.4558	−0.4558	−0.4558
$5\pi_{3/2}$	−0.4307	−0.4326	−0.4326	−0.4326
$5\pi^*_{1/2}$	−0.3700	−0.3719	−0.3719	−0.3719
$5\pi^*_{3/2}$	−0.3477	−0.3501	−0.3501	−0.3501

B. Molecular calculations

In calculations on the I_2 molecule we investigated the effects of the different types of internal Coulomb matrix options. Table III shows the orbital energies of selected orbitals for Dirac–Fock and scaled ZORA basis set calculations. The scaled ZORA results are produced using the full, one-center, and atomic-start-up density Coulomb options. We see that the effects of the use of the different Coulomb options are only visible in the core region. However, even there the differences between the scaled ZORA results are very small and the orbital energies are equally close to the Dirac–Fock ones.

We note that the I_2 molecule is a simple nonpolar example. It might be expected that the cheapest option, the atomic start-up option, does not perform very well in ionic molecules since it uses a Coulomb potential, in the ZORA corrections, based on the superposition of the densities of the neutral atoms.

The orbital energies of the I_2 molecule produced by Dirac–Fock and one-center scaled ZORA calculation are listed in Table IV. Except for the deepest core levels the agreement between Dirac–Fock and scaled ZORA is very good. The deviation of the scaled ZORA results from the Dirac–Fock numbers is of the same order of magnitude as calculated in our numerical xenon calculations. This suggests that the one-center approximation as well as the incompleteness of the internal basis have not resulted in a loss in accuracy. However, it must be noted that the error introduced by the one-center approximation can be much larger for other interatomic distances, Fig. 1. The equilibrium distance (5.33 bohr) displayed in Fig. 1 is obtained from fitting our I_2 data.

The largest spin–orbit splitting can, of course, be found in the 2π orbital. Since the spin–orbit splitting is large and the interaction splitting, i.e., the splitting between gerade and ungerade orbitals, is very small, the observed energy levels should be interpreted as being atomic. The two $2p_{1/2}$ orbitals are combined in the highest 2π orbital, for which the gerade and ungerade combination have the same energy. The remaining $2p_{3/2}$ orbitals are combined in four orbitals, for which the ungerade and gerade combinations are again degenerate. These levels are slightly split by the linear part of the electric field of the nuclei. The spin–orbit splitting calculated with the Dirac–Fock method is 10.94 hartree. It is reproduced by scaled ZORA within 0.15 hartree.

It is remarkable that the absence of splitting between the gerade and ungerade orbitals persists up to the subvalence shell. Only in the valence shell is a significant interaction induced splitting observed.

Table V gives the equilibrium distances for the HI, AgH, AuH, TlH, and Bi_2 molecules at the nonrelativistic, scalar ZORA, and two-component ZORA levels of calculation. Looking at the corresponding one-center and full Coulomb results we can conclude that the one-center approximation has an effect of 0.02–0.03 Å on equilibrium bond lengths of compounds containing a sixth row element (AuH and TlH). This error is of the same magnitude as the error which is usually regarded as allowable in bond length calculations. For Bi_2 the effect is as large as 0.11 Å for scalar ZORA and 0.10 Å for spin–orbit ZORA. Even for the fifth row element Ag, the effect is 0.01 Å. The effect of spin–orbit coupling is only noticeable on the TlH and Bi_2 molecules. For TlH we have a spin–orbit contraction of 0.03 Å for scaled ZORA.

For these molecules we have also computed the harmonic frequencies, Table VI. The spin–orbit effect is pronounced for Bi_2, where we have a decrease of 13 cm^{-1}. For TlH an increase of 51 cm^{-1} is found. The other molecules do not show a significant change. The use of the one-center approximation for the TlH and Bi_2 molecules introduces, except for the scalar ZORA TlH result, an error ranging from 15% to 30%.

Comparing the most accurate ZORA calculations (two-component scaled ZORA with the full Coulomb option) with Dirac–Fock values and experiment, we see that the error made by scaled ZORA compared to experiment is comparable to the error made by Dirac–Fock. This holds for both the equilibrium bond lengths and the harmonic frequencies.

VI. CONCLUSION

The two-component ZORA method has been implemented in the GAMESS-UK package. In atomic calculations we showed that the error of ZORA orbital energies obtained in a basis set calculation, compared to numerical calculations, is of the same order of magnitude as the basis set errors in the corresponding Dirac–Fock calculation. Moreover, we demonstrated that the deviations of the scaled ZORA results from the Dirac–Fock numbers is in every case much smaller than the size of the relativistic effect. The basis

TABLE IV. Orbital energies for the I_2 molecule at 5.0 bohr, obtained with the scaled ZORA method, with the one-center Coulomb matrix option, and the Dirac–Fock method.

	Dirac–Fock	ZORA	ΔE	Dirac–Fock	ZORA	ΔE	
1σ	−1225.9171	−1224.3786	−1.5385	−1225.9171	−1224.3786	−1.5385	$1\sigma^*$
2σ	−193.0169	−192.8346	−0.1823	−193.0169	−192.8346	−0.1823	$2\sigma^*$
	−180.4957	−180.2989	−0.1968	−180.4957	−180.2989	−0.1968	
2π	−169.5547	−169.4884	−0.0662	−169.5547	−169.4884	−0.0662	$2\pi^*$
	−169.5538	−169.4874	−0.0665	−169.5538	−169.4874	−0.0665	
3σ	−40.5096	−40.4772	−0.0325	−40.5096	−40.4772	−0.0325	$3\sigma^*$
	−35.3098	−35.2597	−0.0502	−35.3098	−35.2597	−0.0502	
3π	−33.1988	−33.1951	−0.0036	−33.1988	−33.1951	−0.0036	$3\pi^*$
	−33.1946	−33.1906	−0.0040	−33.1946	−33.1906	−0.0040	
	−24.1560	−24.1520	−0.0040	−24.1560	−24.1520	−0.0040	
	−24.1505	−24.1465	−0.0041	−24.1505	−24.1465	−0.0041	
3δ	−23.7216	−23.7221	0.0005	−23.7216	−23.7221	0.0005	$3\delta^*$
	−23.7193	−23.7198	0.0004	−23.7193	−23.7198	0.0004	
	−23.7146	−23.7150	0.0003	−23.7146	−23.7150	0.0003	
4σ	−7.7508	−7.7458	−0.0050	−7.7507	−7.7458	−0.0050	$4\sigma^*$
	−5.8583	−5.8416	−0.0167	−5.8582	−5.8415	−0.0167	
4π	−5.4490	−5.4541	0.0052	−5.4488	−5.4539	0.0051	$4\pi^*$
	−5.4384	−5.4428	0.0044	−5.4383	−5.4428	0.0044	
	−2.3304	−2.3298	−0.0006	−2.3303	−2.3296	−0.0006	
	−2.3134	−2.3128	−0.0007	−2.3134	−2.3126	−0.0007	
4δ	−2.2655	−2.2686	0.0031	−2.2652	−2.2684	0.0031	$4\delta^*$
	−2.2566	−2.2595	0.0029	−2.2564	−2.2593	0.0029	
	−2.2427	−2.2454	0.0027	−2.2426	−2.2454	0.0027	
5σ	−0.9749	−0.9751	0.0002	−0.8421	−0.8421	−0.0001	$5\sigma^*$
5σ	−0.4678	−0.4645	−0.0033				
$5\pi_{1/2}$	−0.4589	−0.4558	−0.0031	−0.3700	−0.3719	0.0019	$5\pi^*_{1/2}$
$5\pi_{3/2}$	−0.4307	−0.4326	0.0019	−0.3477	−0.3501	0.0024	$5\pi^*_{3/2}$

set error of the employed sets is also much smaller. This brings the calculation on molecules of chemical significance within reach.

For the I_2 molecule it was shown that already a pure atomic ZORA correction is significantly accurate.

In calculations of the equilibrium geometries and harmonic frequencies of the molecules HI, AgH, TlH, AuH and Bi_2, it transpires that the spin–orbit effect on the bond lengths is only noticeable in the TlH and Bi_2 molecules.

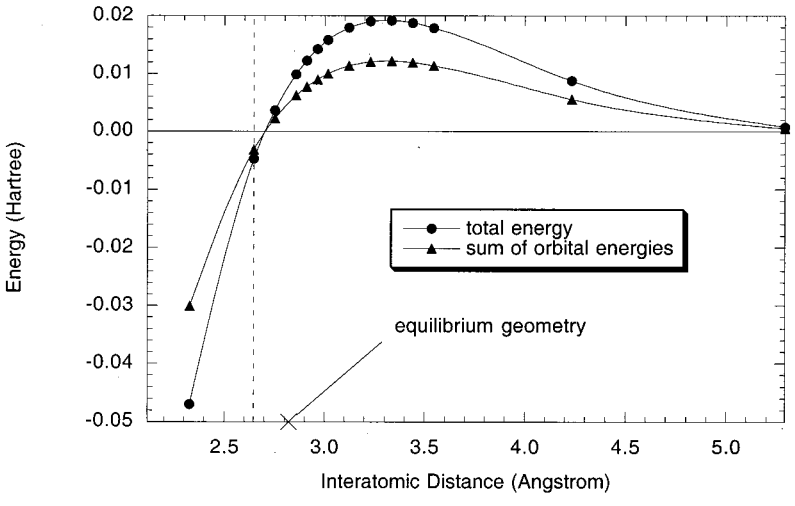

FIG. 1. Error made by the one-center Coulomb option with respect to the full Coulomb option with the scaled ZORA method for the I_2 molecule. The vertical dashed line indicates the geometry used in Tables III and IV.

TABLE V. Equilibrium distances (Å) from nonrelativistic, scalar (sr), and two-component (tc) scaled ZORA (using the one-center and full Coulomb option) calculations. Comparison with experiment and Dirac–Fock values.

		AgH	HI	AuH	TlH	Bi_2
Non-Rel.		1.74	1.61	1.78	1.93	2.61
sr ZORA	One center	1.68	1.60	1.65	1.93	2.64
tc ZORA	One center	1.68	1.60	1.65	1.92	2.63
sr ZORA	Full	1.67	1.60	1.62	1.91	2.53
tc ZORA	Full	1.67	1.60	1.62	1.88	2.53
Dirac–Fock		1.67	1.60	1.62	1.87	2.59
Experiment		1.617[a]	1.608[a]	1.5237[a]	1.87[a]	2.66[b]

[a]Reference 18.
[b]Reference 19.

Upon inclusion of spin–orbit coupling the calculated bond length for TlH decreases with 0.03 Å.

The effect of the one-center approximation on the bond lengths is about 0.03 Å for compounds containing one sixth row element. For Bi_2 the errors are 0.11 and 0.10 Å for scalar and two-component ZORA, respectively. In the computation of harmonic frequencies, the one-center approximation produces a serious error in the TlH and Bi_2 molecules. These deviations are a result of the variation of the error introduced by the one-center approximation with the bond distance, Fig. 1. It can be concluded that the one-center approximation can only be used in systems with only one fifth row atom.

For the systems considered, the two-component scaled ZORA method is able to achieve the same degree of accuracy as is obtained using the full four-component Dirac–Fock method. These results suggest that the two-component scaled ZORA approach is a cost-effective alternative to Dirac–Fock for the calculation of potential energy surfaces.

TABLE VI. Harmonic frequencies (cm^{-1}) from nonrelativistic, scalar (sr), and two-component (tc) scaled ZORA (using the one-center and full Coulomb option) calculations. Comparison with experiment and Dirac–Fock values.

		AgH	HI	AuH	TlH	Bi_2
Nonrel.		1561	2421	1608	1534	238
sr ZORA One center	One	1693	2432	2110	1459	293
tc ZORA	One center	1694	2431	2110	1631	301
sr ZORA	Full	1752	2349	1979	1397	240
tc ZORA	Full	1751	2346	1978	1448	227
Dirac–Fock		1691	2426	1981	1477	191
Experiment[a]		1760	2309	2305	1391	173

[a]Reference 19.

For ionization potentials the method gives acceptable results except for the deepest levels, e.g., the $1s$ and $2sp$ shells of radon. The suitability of ZORA for other properties requires further investigation.

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[1] P. Pyykkö, Chem. Rev. **88**, 563 (1988).
[2] Ch. Chang, M. Pelissier, and Ph. Durand, Phys. Scr. **34**, 394 (1986).
[3] J.-L. Heully, I. Lindgren, E. Lindroth, S. Lundquist, and A.-M. Mårtensson-Pendrill, J. Phys. B **19**, 2799 (1986).
[4] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **99**, 4597 (1993).
[5] E. van Lenthe, E. J. Baerends, and J. G. Snijders, J. Chem. Phys. **101**, 1272 (1994).
[6] S. Faas, J. G. Snijders, J. H. van Lenthe, E. van Lenthe, and E. J. Baerends, Chem. Phys. Lett. **246**, 632 (1995).
[7] S. Faas, J. G. Snijders, and J. H. van Lenthe, *Quantum Systems in Chemistry and Physics*, Basic Problems and Model Systems, Vol. 1 (Kluwer Academic, Dordrecht, 2000), p. 251.
[8] A. J. Sadlej, J. G. Snijders, E. van Lenthe, and E. J. Baerends, J. Chem. Phys. **102**, 1758 (1995).
[9] GAMESS-UK is a package of *ab initio* programs written by M. F. Guest, J. H. van Lenthe, J. Kendrick, K. Schoffel, P. Sherwood, and R. J. Harrison, with contributions from R. D. Amos, R. J. Buenker, M. Dupuis, N. C. Handy, I. H. Hillier, P. J. Knowles, V. Bonacic-Koutecky, W. von Niessen, V. R. Saunders, and A. J. Stone. The package is derived from the original GAMESS code due to M. Dupuis, D. Spangler, and J. Wendoloski, NRCC Software Catalog, Vol. 1, Program No. QG01 (GAMESS) (1980).
[10] F. A. Parpia, I. P. Grant, and C. F. Fischer, Comput. Phys. Commun. **94**, 249 (1996).
[11] L. Visscher, O. Visser, P. J. C. Aerts, H. Merenga, and W. C. Nieuwpoort, Comput. Phys. Commun. **81**, 120 (1994).
[12] ''DIRAC, a relativistic *ab initio* electronic structure program, Release 3.1 (1998),'' T. Saue, T. Enevoldsen, T. Helgaker, H. J. Aa. Jensen, J. K. Laerdahl, K. Ruud, J. Thyssen, and L. Visscher (http://dirac.chem.sdu.dk).
[13] E. van Lenthe, R. van Leeuwen, E. J. Baerends, and J. G. Snijders, Int. J. Quantum Chem. **57**, 281 (1996).
[14] S. Huzinaga, J. Andzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations* (Elsevier, Amsterdam, 1984).
[15] K. G. Dyall, Theor. Chem. Acc. **99**, 366 (1998).
[16] R. Poirier, R. Kari, and I. G. Csizmadia, *Handbook of Gaussian Basis Sets, a Compendium for Ab Initio Molecular Orbital Calculations* (Elsevier, Amsterdam, 1985).
[17] J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc. **102**, 939 (1980).
[18] *Table of Interatomic Distances and Configuration in Molecules and Ions*, edited by A. D. Mitchell and L. C. Cross (Thanet, Markate, Kent, UK, 1958).
[19] K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).