An Implementation
of the Scalar Relativistic Density Functional Theory
for Molecular Calculations with Gaussian Basis Sets

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1 Introduction

The importance of the so-called relativistic effects for accurate description of molecules containing more or less heavy elements is well understood and documented [1]. In view of continuous progress in developing Dirac-Fock based correlated electronic structure methods such as CCSD(T) [2], it is remarkable that four-component density functional methods are only recently becoming available. On the other hand the first four-component density functional calculations (within the Dirac-Slater model) were reported as early as in 1975 [3]. There can be several reasons that prevent the wide use of four-component formalisms in quantum chemistry. Whereas almost all nonrelativistic calculations are done in real numbers, complex numbers are inevitable in the four-component case. Together with at least twice larger dimension of the eigenvalue problem (because of coupling of α- and β-spins) this may lead to much higher computational requirements. There is also a problem particular to approximate density functional methods: most commonly used exchange-correlation functionals depend explicitly upon the spin density, but in the four-component case only the total density is rotationally invariant, so the spin-unpolarized versions of the functionals should be used which are less accurate for systems with unpaired electrons. With this in mind it may appear useful to have a scalar-relativistic approach which would take into account the most important relativistic kinematic effects but would allow the separation of spins and the use of real arithmetic. This can be done by an exact separation of scalar and spin-orbit contributions [4], even though there is some controversy about its uniqueness [5]. In this work the computational efficiency of a preliminary implementation of the scalar relativistic density functional theory within a Gaussian basis set approach is estimated.

2 Theory

Molecular calculations based on the one-electron Dirac Hamiltonian

$$\hat{h} = \begin{pmatrix} 0 & c\,\hat{\sigma}\cdot\hat{p} \\ c\,\hat{\sigma}\cdot\hat{p} & -2c^2 \end{pmatrix} + v(\mathbf{r}), \tag{1}$$

where

$$\hat{\sigma}\cdot\hat{p} = \begin{pmatrix} \hat{p}_z & \hat{p}_x - i\hat{p}_y \\ \hat{p}_x + i\hat{p}_y & -\hat{p}_z \end{pmatrix}, \tag{2}$$

can be conveniently performed within a basis set approach that begins with some set of primitive scalar functions $\{g_m(\mathbf{r})\}$ from which a contracted four-component basis set $\{\chi_\mu(\mathbf{r})\}$ is built. It can be chosen to contain functions of α- and β-spin:

$$\chi_\mu^\alpha = \begin{pmatrix} \chi_\mu^{0\alpha} \\ \chi_\mu^{1\alpha} \end{pmatrix}, \qquad \chi_\mu^\beta = \begin{pmatrix} \chi_\mu^{0\beta} \\ \chi_\mu^{1\beta} \end{pmatrix}, \tag{3}$$

with the large components as in the nonrelativistic case:

$$\chi_\mu^{0\alpha} = c_{m\mu}^0 \begin{pmatrix} g_m \\ 0 \end{pmatrix}, \qquad \chi_\mu^{0\beta} = c_{m\mu}^0 \begin{pmatrix} 0 \\ g_m \end{pmatrix}, \tag{4}$$

and the small components formed by contracting corresponding kinetically-balanced primitive functions:

$$\chi_\mu^{1\alpha} = \frac{c_{m\mu}^1}{2c} \begin{pmatrix} ig_m^z \\ ig_m^x - g_m^y \end{pmatrix}, \qquad \chi_\mu^{1\beta} = \frac{c_{m\mu}^1}{2c} \begin{pmatrix} ig_m^x + g_m^y \\ -ig_m^z \end{pmatrix}, \tag{5}$$

where g_m^x, g_m^y and g_m^z are Cartesian derivatives, for example $g_m^z = \partial g_m/\partial z$. The large and small component contraction coefficients $c_{m\mu}^0$ and $c_{m\mu}^1$ should be chosen in an atomically-balanced way — then the approach is variationally stable for molecules as well. It is trivial to see that the products of the basis functions have the form:

$$\chi_\mu^{\alpha\dagger}\chi_\nu^\alpha = \bar{c}_{m\mu}^0 c_{n\nu}^0 \bar{g}_m g_n + \frac{\bar{c}_{m\mu}^1 c_{n\nu}^1}{4c^2} \left(\nabla\bar{g}_m \cdot \nabla g_n + i(\bar{g}_m^x g_n^y - \bar{g}_m^y g_n^x) \right), \tag{6}$$

$$\chi_\mu^{\beta\dagger}\chi_\nu^\beta = \bar{c}_{m\mu}^0 c_{n\nu}^0 \bar{g}_m g_n + \frac{\bar{c}_{m\mu}^1 c_{n\nu}^1}{4c^2} \left(\nabla\bar{g}_m \cdot \nabla g_n - i(\bar{g}_m^x g_n^y - \bar{g}_m^y g_n^x) \right), \tag{7}$$

$$\chi_\mu^{\alpha\dagger}\chi_\nu^\beta = \frac{\bar{c}_{m\mu}^1 c_{n\nu}^1}{4c^2} \left((\bar{g}_m^z g_n^x - \bar{g}_m^x g_n^z) + i(\bar{g}_m^y g_n^z - \bar{g}_m^z g_n^y) \right). \tag{8}$$

It is easy to identify the last terms in Eqns. (6) and (7) and the whole Eqn. (8) as the spin-orbit contributions, whereas the $\nabla \bar{g}_m \cdot \nabla g_n$ terms are the scalar relativistic contributions.

All the required matrix elements can be easily computed in terms of simple integrals over primitive basis functions. The overlap and kinetic energy integrals are:

$$S_{\mu\nu} = \bar{c}^0_{m\mu} c^0_{n\nu} S_{mn} + \frac{\bar{c}^1_{m\mu} c^1_{n\nu}}{2c^2} T_{mn}, \qquad (9)$$

$$T_{\mu\nu} = \left(\bar{c}^0_{m\mu} c^1_{n\nu} + \bar{c}^1_{m\mu} c^0_{n\nu} - \bar{c}^1_{m\mu} c^1_{n\nu} \right) T_{mn}, \qquad (10)$$

where

$$S_{mn} = \int \bar{g}_m(\mathbf{r}) g_n(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \qquad T_{mn} = \tfrac{1}{2} \int \nabla \bar{g}_m(\mathbf{r}) \cdot \nabla g_n(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \qquad (11)$$

The scalar relativistic matrix elements of a local potential are:

$$V_{\mu\nu} = \bar{c}^0_{m\mu} c^0_{n\nu} V_{mn} + \frac{\bar{c}^1_{m\mu} c^1_{n\nu}}{4c^2} V^{11}_{mn}, \qquad (12)$$

with

$$V_{mn} = \int v(\mathbf{r}) \bar{g}_m(\mathbf{r}) g_n(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \qquad V^{11}_{mn} = \int v(\mathbf{r}) \nabla \bar{g}_m(\mathbf{r}) \cdot \nabla g_n(\mathbf{r}) \, \mathrm{d}\mathbf{r}, \quad (13)$$

whereas the additional spin-orbit terms (if desired) can be easily evaluated as:

$$V^{\alpha\alpha}_{\mu\nu} = -V^{\beta\beta}_{\mu\nu} = \frac{\bar{c}^1_{m\mu} c^1_{n\nu}}{4c^2} \mathrm{i} V^{xy}_{mn}, \qquad V^{\alpha\beta}_{\mu\nu} = \frac{\bar{c}^1_{m\mu} c^1_{n\nu}}{4c^2} (\mathrm{i} V^{yz}_{mn} + V^{zx}_{mn}), \qquad (14)$$

with

$$V^{xy}_{mn} = \int v(\mathbf{r}) \left(\bar{g}^x_m(\mathbf{r}) g^y_n(\mathbf{r}) - \bar{g}^y_m(\mathbf{r}) g^x_n(\mathbf{r}) \right) \, \mathrm{d}\mathbf{r}, \qquad (15)$$

and in the same way for V^{yz}_{mn} and V^{zx}_{mn}.

The potential $v(\mathbf{r})$ can be either nuclear, Coulomb or exchange-correlation potential as needed in density functional calculations. Nonrelativistic gradient-corrected models can be used to a good approximation in the scalar relativistic calculations.

3 Implementation

In the implementation of this work the Coulomb and exchange-correlation energies are treated using the resolution-of-the-identity approximation, within which the density is re-expanded in an auxiliary basis set $\{\eta_m(\mathbf{r})\}$:

$$\rho(\mathbf{r}) = D_{\mu\nu}\chi_\mu^\dagger(\mathbf{r})\chi_\nu(\mathbf{r}) \approx \tilde{\rho}(\mathbf{r}) = d_m\eta_m(\mathbf{r}). \tag{16}$$

Expansion coefficients are determined from the linear equations:

$$(m|n)d_n = (m|\mu\nu)D_{\mu\nu}, \tag{17}$$

where the Coulomb integrals $(m|\mu\nu)$ in the scalar relativistic case are computed according to Eqn. (12). The Coulomb and exchange-correlation energies are then evaluated over the approximate density

$$\tilde{J} = \tfrac{1}{2}d_m(m|n)d_n, \tag{18}$$

$$\tilde{E}_{\text{xc}} = \int e_{\text{xc}}(\tilde{\rho}_\alpha(\mathbf{r}), \tilde{\rho}_\beta(\mathbf{r}), \nabla\tilde{\rho}_\alpha(\mathbf{r}), \nabla\tilde{\rho}_\beta(\mathbf{r}))\,\mathrm{d}\mathbf{r}. \tag{19}$$

Expressions for the matrix elements of the Coulomb and exchange-correlation potentials as well as the second order response terms are easy to derive in the way consistent with these approximations. The approach on the whole parallels its nonrelativistic analogue [6].

The integral routines are optimized for processing generally-contracted Gaussian basis sets with shared exponents and are based on the McMurchie-Davidson algorithm [7]. The Gaussian finite nuclear model [8] is used in evaluating the nuclear potential integrals. The SCF equations are solved by the quadratically-convergent method in which the second-order response contributions are computed neglecting small-component terms — this does not degrade the convergence and allows appreciable time savings. Analytic energy gradients with respect to nuclear positions are available for geometry optimizations.

The generalized gradient approximation of Perdew-Burke-Ernzerhof [9] has been chosen in this work due to its sound theoretical derivation and simple analytical form free of adjustable parameters.

4 Applications

To estimate the performance of the present approach geometry optimizations have been performed for two moderately large molecules: a binuclear uranium complex $[U_2H_4(C_5H_5)_4]$ (fig. 1), known as an alkene hydrogenation catalyst, and its adduct with ethylene $[(C_2H_4)U_2H_4(C_5H_5)_4]$ (fig. 2).

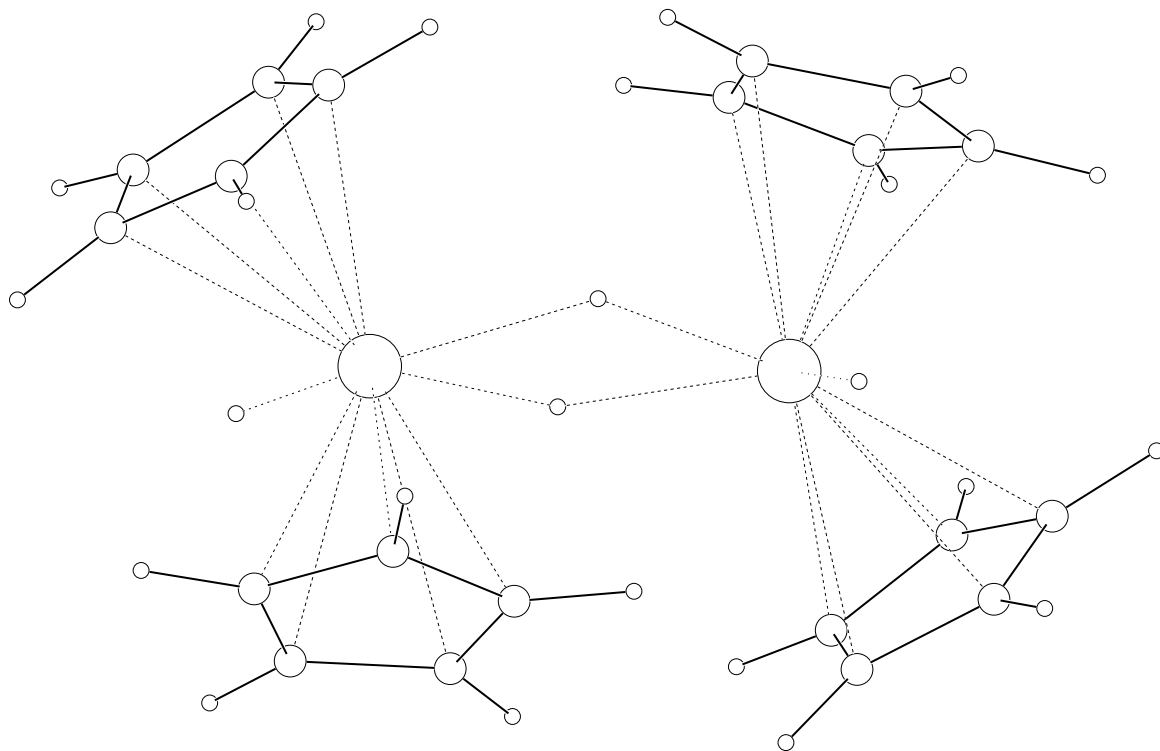
Figure 1: complex $[U_2H_4(C_5H_5)_4]$

The generally-contracted atomic basis sets have the dimensions: (5s1p)/[3s1p] for H, (11s6p2d)/[4s3p2d] for C, (27s25p18d13f)/[9s8p6d4f] for U and are derived from the primitive basis sets optimized in spherically-averaged atomic calculations. Generally-contracted auxiliary basis sets have the dimensions: (4s1p)/[3s1p] for H, (8s3p3d1f)/[5s2p2d1f] for C, (25s9p9d8f8g7h7i)/[20s5p5d4f4g3h3i] for U and are optimized to represent the one-center products of the primary basis functions. The total number of primary (auxiliary) basis functions is 856 (1176) for the larger molecule.

The calculations have been performed on a two-processor 350MHz Pentium-II computer using the parallelized version of the code. On the average, one cycle of geometry optimization took 2–3 hours of wall time. For these particular systems the convergence of SCF process is rather slow, and on the first geometry up to 8 hours were necessary. About 50% of the
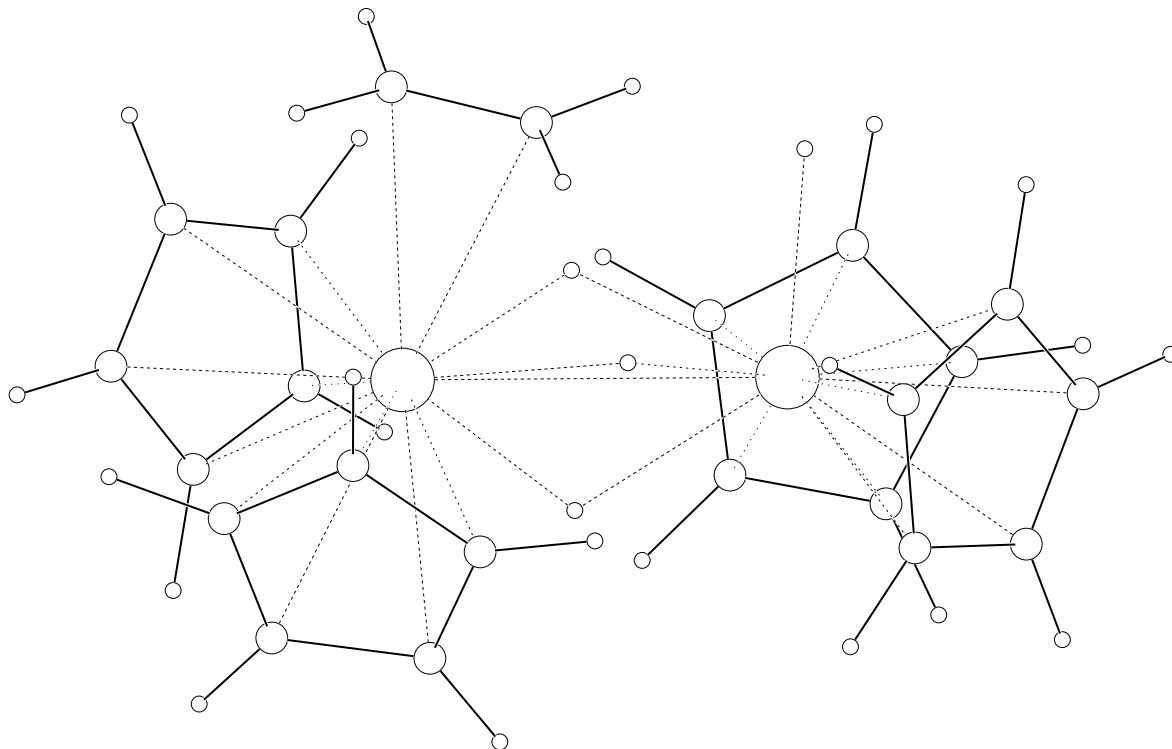
Figure 2: complex $[(C_2H_4)U_2H_4(C_5H_5)_4]$

CPU time corresponds to the formation of the Coulomb-type integrals, 30% to numerical integration of the exchange-correlation contributions, 17% to the matrix multiply and about 3% to the sequential diagonalization which is used at the beginning and at the end of the SCF process.

The calculations predict quintet ground state for both complexes which is consistent with the f^2-f^2 effective configuration of the metal centers. The binding energy of ethylene is predicted to be 23.2 kcal/mol. Further studies may lead to a detailed picture of the catalytic hydrogenation process.

5   Conclusions

The scalar relativistic approach implemented in this work seems to be quite inexpensive and can be used for structure optimizations for molecules of moderate size. We hope that after further testing and debugging the computer code developed will be made available to interested researchers in the near future.

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