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► **To cite this version:**

Miroslav Iliáš, Trond Saue. An infinite-order two-component relativistic Hamiltonian by a simple one-step transformation. *The Journal of Chemical Physics*, 2007, 126 (6), pp.064102. 10.1063/1.2436882 . hal-03327453

HAL Id: hal-03327453

<https://hal.science/hal-03327453v1>

Submitted on 27 Aug 2021

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An infinite-order two-component relativistic Hamiltonian by a simple one-step transformation

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(Received 13 November 2006; accepted 3 January 2007; published online 13 February 2007)

The authors report the implementation of a simple one-step method for obtaining an infinite-order two-component (IOTC) relativistic Hamiltonian using matrix algebra. They apply the IOTC Hamiltonian to calculations of excitation and ionization energies as well as electric and magnetic properties of the radon atom. The results are compared to corresponding calculations using identical basis sets and based on the four-component Dirac-Coulomb Hamiltonian as well as Douglas-Kroll-Hess and zeroth-order regular approximation Hamiltonians, all implemented in the DIRAC program package, thus allowing a comprehensive comparison of relativistic Hamiltonians within the finite basis approximation. © 2007 American Institute of Physics.

[DOI: 10.1063/1.2436882]

I. INTRODUCTION

Whereas it is generally acknowledged that the inclusion of relativistic effects is crucial for the theoretical description of the chemistry of heavy elements,¹ there is less consensus as to how to introduce such effects in actual calculations. Within the Born-Oppenheimer approximation all electronic Hamiltonians, relativistic or not, have the generic form

$$\hat{H} = \sum_i \hat{h}(i) + \frac{1}{2} \sum_{i \neq j} \hat{g}(i, j) + V_{NN}, \quad (1)$$

where V_{NN} is the classical repulsion of clamped nuclei and where \hat{h} and \hat{g} are one- and two-electron operators, respectively. This common form is usually sufficient to define and derive the various electronic structure methods of quantum chemistry, which implies that they can be extended to the relativistic domain, although various technical issues may have to be tackled.^{2,3}

The present most rigorous treatment employed in quantum chemistry is based on the four-component Dirac-Coulomb-Breit/Gaunt Hamiltonian, which is obtained by selecting the Dirac operator in the molecular field as the one-electron operator \hat{h} and the Coulomb term, possibly extended by the Gaunt or Breit terms, as the two-electron operator \hat{g} . The introduction of the complex algebra and the reduced symmetry associated with the spin-orbit interaction leads theoretically to a prefactor on the order of 10 compared to the cost of a nonrelativistic calculation. The introduction of a separate basis set for small components introduces an additional factor of 10. These computational bottlenecks limit the

application of four-component Hamiltonians to small- and medium-sized chemical systems only. There has, however, been considerable progress in reducing the cost of such calculations, for instance, by integral screening,⁴ density fitting,⁵⁻⁷ pseudospectral methods,⁸ and symmetry schemes that exploit maximally nonrelativistic symmetry in the presence of spin-orbit coupling.⁹ A major breakthrough was the introduction by Visscher of a simple energy correction that completely eliminated the two-electron Coulomb integrals involving the small components only.¹⁰ Further progress along these lines has been reported by Pedersen.¹¹ Recently, Liu and Peng¹² demonstrated how the cost of four-component relativistic density functional theory (DFT) calculations can be made identical to that of two-component calculations by the introduction of model atomic densities for the small components. Beyond a four-index transformation, e.g., at the coupled cluster (CC) or configuration interaction (CI) level, the cost of two- and four-component calculations is strictly identical since the negative-energy solutions are not included in such calculations.

The high computational cost traditionally associated with four-component relativistic calculations has motivated the development of computationally less demanding two-component Hamiltonians. Two-component relativistic Hamiltonians, involving only positive-energy orbitals, can be divided into pseudopotential and all-electron methods. The latter group consists of a plethora of two-component Hamiltonians accurate to various orders in some expansion parameter.

One of the most popular two-component Hamiltonians is the second-order Douglas-Kroll-Hess¹³⁻¹⁵ (DKH) Hamiltonian. Closely related is the Hamiltonian proposed by Barysz *et al.*¹⁶ Barysz and Sadlej.¹⁷ In both cases a free-

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particle Foldy-Wouthuysen (FW) transformation is first applied to the Dirac operator. The subsequent coupling equation is then expanded in the external potential and the fine-structure constant α , giving the DKH and Barysz-Sadlej-Snidars (BSS) Hamiltonians, respectively.¹⁷ Another widely used Hamiltonian, particularly in a DFT framework, is the zeroth-order regular approximation (ZORA) Hamiltonian^{18–20} and variants hereof. These Hamiltonians are variationally stable in the sense²¹ that they have a lower bound which, however, need not be exactly the lower positive-energy solution of the corresponding Dirac operator and may even be slightly below. Spin-free one-component forms of these Hamiltonians are easily incorporated into nonrelativistic quantum chemical machinery through a modification of one-electron atomic integrals. On the other hand, the rigorous handling of both scalar relativistic and spin-orbit effects requires a dedicated code.

A scheme for obtaining an arbitrary (including infinite) order two-component relativistic Hamiltonian was proposed by Barysz and Sadlej.²² High-order DKH Hamiltonians have, on the other hand, been proposed by Nakajima and Hirao,²³ van Wüllen,²⁴ as well as Reiher and Wolf.^{25,26} However, all the above mentioned works share a common feature: Two-component Hamiltonians are derived at the operator level and only at a later stage are matrix elements over the final operator expressions programmed. However, approximate Hamiltonians can be obtained in a much simpler manner by matrix manipulations starting directly from the Dirac operator in the finite basis approximation. Such a scheme was proposed by Dyall as early as 1997.²⁷ More recently, Jensen and Iliaš²⁸ have translated the scheme for generating the BSS Hamiltonian into matrix algebra. The iterative solution of an operator equation is then replaced by direct diagonalization followed by the solution of a system of linear equations. Spectroscopic constants for the PbO molecule and its anion using this Hamiltonian were reported in Ref. 29. A similar and more general scheme has been actively pursued by Liu and Peng¹² and by Kutzelnigg and Liu^{30,31} under the name of exact quasirelativistic (XQR) theory.

In this paper we report the implementation of a very simple scheme for obtaining an infinite-order two-component (IOTC) relativistic Hamiltonian. We will use the acronym IOTC, introduced by Kędziera and Barysz,³² since it describes precisely the object that we seek a matrix representation of. We have employed a development version of the DIRAC program suite,³³ which means that our IOTC Hamiltonian can be immediately used with a wide range of methods, including Hartree-Fock (HF),^{4,9} DFT,³⁴ second-order Møller-Plesset perturbation theory (MP2),³⁵ multiconfiguration self-consistent field³⁶ (SCF) as well as CI^{37,38} and CC^{39,40} methods. An outstanding advantage of the matrix algebra approach is that an explicit matrix representation of the decoupling transformation is generated and can be applied on the fly to property operators such that picture change errors^{41–43} are completely avoided. Using DIRAC, we can therefore calculate expectation values, linear⁴⁴ and quadratic response⁴⁵ functions for a wide range of electric and magnetic properties, currently at the HF and DFT levels.

Our paper is organized as follows: In Sec. II we first

show the equivalence of two approaches for the generation of two-component relativistic Hamiltonians, namely, the elimination of the small components and Foldy-Wouthuysen transformations. This allows us to focus exclusively on the generation of such Hamiltonians by sequences of unitary transformations. We briefly establish links to various finite-order schemes and then present our one-step method for obtaining the IOTC Hamiltonian. Details concerning the implementation are found in Sec. III. We report pilot calculations on the radon atom in Secs. IV and V. It should be stressed, though, that molecular calculations are perfectly feasible. We conclude and provide perspectives in Sec. VI.

II. THEORY

Our point of departure is the Dirac equation in a molecular field,

$$\begin{bmatrix} V & c(\boldsymbol{\sigma} \cdot \mathbf{p}) \\ c(\boldsymbol{\sigma} \cdot \mathbf{p}) & V - 2mc^2 \end{bmatrix} \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} = \begin{bmatrix} \psi^L \\ \psi^S \end{bmatrix} E, \quad (2)$$

where $V = -\phi(\mathbf{r})$ describes the interaction of an electron with the electrostatic potential of the clamped nuclei. This equation has solutions of both positive and negative energy. It should be emphasized, since this is repeatedly misunderstood in the literature, that *all* solutions are electronic since the introduction of potential by the principle of minimal electromagnetic coupling⁴⁶ requires a specification of charge.² For chemical purposes one chooses the charge of the electron $q = -1$ a.u. and not the charge of the positron. This interpretation is in agreement with Dirac himself,⁴⁷ who pointed out that negative-energy positrons would be in conflict with experiment, and is crucial for understanding the extension to the quantum field theory. The observable positronic solutions in the same potential are obtained by explicitly choosing positron charge when coupling to the potential or by charge conjugation of the negative-energy solutions of the electronic problem.

In the literature two main approaches have been considered for the decoupling of the positive and negative-energy solutions of this equation: (i) elimination of the small components (ESC) and (ii) unitary decoupling transformation, generally referred to as a FW transformation. We will show that these approaches are equivalent, which then allows us to focus exclusively on the FW transformation.

A. Elimination of the small components

Consider first the elimination of small components. We write the Dirac equation as a system of coupled equations,

$$\hat{h}_{11}\psi^L + \hat{h}_{12}\psi^S = E\psi^L, \quad (3)$$

$$\hat{h}_{21}\psi^L + \hat{h}_{22}\psi^S = E\psi^S, \quad (4)$$

in obvious notation. Let the operator \hat{R} be the exact coupling of the large and small components

$$\psi^S = \hat{R}\psi^L. \quad (5)$$

In the first step we eliminate the small components in Eq. (3),

$$[\hat{h}_{11} + \hat{h}_{12}\hat{R}] \psi^L = E \psi^L. \quad (6)$$

The second step is renormalization, alternative introduction of a metric. If the point of departure is a normalized four-component wave function, the large components are not normalized to unity by themselves. Introducing $\phi = \hat{N}_+ \psi^L$, the normalization operator \hat{N}_+ is extracted from

$$\langle \phi | \phi \rangle = \langle \psi^L | \psi^L \rangle = \langle \psi^L | 1 + \hat{R}^\dagger \hat{R} | \psi^L \rangle \Rightarrow \hat{N}_+ = \sqrt{1 + \hat{R}^\dagger \hat{R}}, \quad (7)$$

where we have used the coupling relation [Eq. (5)]. The final Hamiltonian for the two-component wave function ϕ thereby becomes

$$\begin{aligned} \hat{h}_+ &= \hat{N}_+ [\hat{h}_{11} + \hat{h}_{12}\hat{R}] \hat{N}_+^{-1} \\ &= \sqrt{1 + \hat{R}^\dagger \hat{R}} [\hat{h}_{11} + \hat{h}_{12}\hat{R}] \frac{1}{\sqrt{1 + \hat{R}^\dagger \hat{R}}}. \end{aligned} \quad (8)$$

$$\begin{bmatrix} \hat{h}_{11} + \hat{h}_{12}\hat{R} + \hat{R}^\dagger \hat{h}_{21} + \hat{R}^\dagger \hat{h}_{22}\hat{R} & -\hat{h}_{11}\hat{R}^\dagger + \hat{h}_{12} - \hat{R}^\dagger \hat{h}_{21}\hat{R} + \hat{R}^\dagger \hat{h}_{22} \\ -\hat{R}\hat{h}_{11} - \hat{R}\hat{h}_{12}\hat{R} + \hat{h}_{21} + \hat{h}_{22}\hat{R} & \hat{R}\hat{h}_{11}\hat{R}^\dagger - \hat{R}^\dagger \hat{h}_{12} - \hat{h}_{21}\hat{R}^\dagger + \hat{h}_{22} \end{bmatrix}. \quad (11)$$

The off-diagonal elements are connected by Hermitian conjugation and should be zero in the case of exact decoupling. This implies

$$\hat{h}_{21} + \hat{h}_{22}\hat{R} = \hat{R}\hat{h}_{11} + \hat{R}\hat{h}_{12}\hat{R}, \quad (12)$$

a relation that is *only* valid for the exact \hat{R} . The second transformation \hat{W}_2 introduces renormalization, thus ensuring the unitarity of the transformation. In this final step we obtain the Hamiltonian for the positive-energy states

$$\hat{h}_+ = \frac{1}{\sqrt{1 + \hat{R}^\dagger \hat{R}}} [\hat{h}_{11} + \hat{h}_{12}\hat{R} + \hat{R}^\dagger (\hat{h}_{21} + \hat{h}_{22}\hat{R})] \frac{1}{\sqrt{1 + \hat{R}^\dagger \hat{R}}}, \quad (13)$$

which is identical to Eq. (8) when we use the coupling equation [Eq. (12)]. We have therefore shown the equivalence of the elimination of the small components and the Foldy-Wouthuysen transformation when \hat{R} is the *exact* coupling between the large and small components.

The connection is made even more explicit when we consider the decoupling transformation [Eq. (10)] of the matrix of eigenvectors, which gives

$$\begin{bmatrix} \tilde{\psi}_+^L & \tilde{\psi}_-^L \\ \tilde{\psi}_+^S & \tilde{\psi}_-^S \end{bmatrix} = \hat{W}_2 \begin{bmatrix} \psi_+^L + \hat{R}^\dagger \psi_+^S & \psi_-^L + \hat{R}^\dagger \psi_-^S \\ \psi_+^S - \hat{R} \psi_+^L & \psi_-^S - \hat{R} \psi_-^L \end{bmatrix}. \quad (14)$$

We seek $\tilde{\psi}_+^S = 0$ and $\tilde{\psi}_-^L = 0$, which implies

B. Foldy-Wouthuysen transformation

We seek a unitary transformation \hat{U} to decouple solutions of positive and of negative energy,

$$\hat{U}^\dagger \begin{bmatrix} \hat{h}_{11} & \hat{h}_{12} \\ \hat{h}_{21} & \hat{h}_{22} \end{bmatrix} \hat{U} = \begin{bmatrix} \hat{h}_+ & 0 \\ 0 & \hat{h}_- \end{bmatrix}. \quad (9)$$

The general form of this transformation was first given by Heully *et al.*⁴⁸ Kutzelnigg,^{49,50} has emphasized the utility of writing it as the product of two transformations,

$$\hat{U} = \hat{W}_1 \hat{W}_2: \quad \hat{W}_1 = \begin{bmatrix} 1 & -\hat{R}^\dagger \\ \hat{R} & 1 \end{bmatrix}, \quad (10)$$

$$\hat{W}_2 = \begin{bmatrix} \hat{N}_+^{-1} & 0 \\ 0 & \hat{N}_-^{-1} \end{bmatrix}, \quad \hat{N}_+ = \sqrt{1 + \hat{R}^\dagger \hat{R}}, \quad \hat{N}_- = \sqrt{1 + \hat{R} \hat{R}^\dagger}.$$

The first transformation \hat{W}_1 provides decoupling, giving

$$\psi_+^S = \hat{R} \psi_+^L, \quad \psi_-^L = -\hat{R}^\dagger \psi_-^S, \quad (15)$$

from which one sees that \hat{R} couples the large and small positive-energy eigenvectors. The final renormalized nonzero two-component functions read

$$\tilde{\psi}_+^L = \sqrt{1 + \hat{R}^\dagger \hat{R}} \psi_+^L, \quad \tilde{\psi}_-^S = \sqrt{1 + \hat{R} \hat{R}^\dagger} \psi_-^S. \quad (16)$$

A subtle feature, first discussed by Heully *et al.*,⁴⁸ should be pointed out: the exact coupling of the large and small components of the Dirac equation [Eq. (2)] can be expressed as

$$\hat{R} = \frac{1}{2mc} \hat{B}(E) (\boldsymbol{\sigma} \cdot \mathbf{p}), \quad \hat{B}(E) = \left[1 + \frac{E - V}{2mc^2} \right]^{-1}. \quad (17)$$

This is, however, an energy-dependent, and thus *state-specific*, coupling. Heully *et al.*⁴⁸ developed a *state-universal* quadratic equation. Repeating this exercise in a kinetically balanced basis, one obtains the coupling equation that forms the basis of the iterative XQR scheme proposed by Kutzelnigg and Liu.³⁰ Heully *et al.*⁴⁸ also pointed out that the coupling operator \hat{R} will be different for positive- and negative-energy solutions, a feature that is seen from Eq. (15). In Eq. (5) above we have not specified whether \hat{R} refers to the state-specific or state-universal coupling operator. Unless explicitly or otherwise indicated, \hat{R} in this paper will refer to the state-universal coupling operator, in conformity with the notation used in the paper by Heully *et al.*⁴⁸ In practice, this distinction may not be that crucial since the coupling

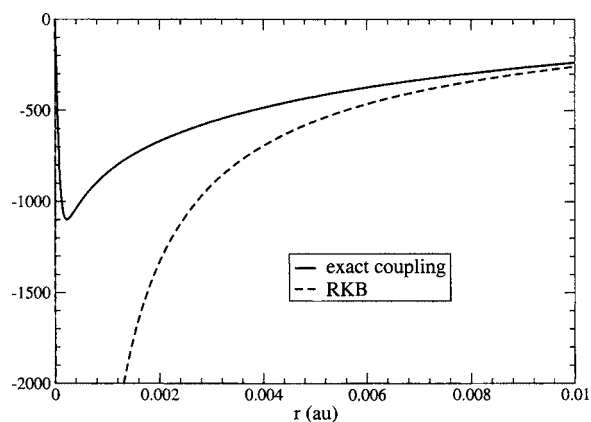


FIG. 1. The small component radial function of the radon atom, obtained from a four-component relativistic Hartree-Fock calculation with the atomic GRASP code (Ref. 82), compared to the function obtained by the application of the nonrelativistic coupling [Eq. (20)] on the large radial function. The root-mean-square radius of the radon nucleus is of the order of 10^{-4} a.u. (Ref. 76) and the radial expectation value $\langle r \rangle$ of the $1s_{1/2}$ orbital is 1.5×10^{-2} a.u..

transformations may be carried out starting from the *time-dependent* Dirac equation, in which no explicit energy appears. This is, for instance, shown by Moss,⁵¹ who obtains identical Hamiltonians using the method of elimination of small components and Foldy-Wouthuysen transformations.

Finally, one may note that the final working equation

$$\hat{h}_+ \tilde{\psi}_+^L = E \tilde{\psi}_+^L \quad (18)$$

can be rearranged to

$$[\hat{h}_{11} + \hat{h}_{12} \hat{R} + \hat{R}^\dagger (\hat{h}_{21} + \hat{h}_{22} \hat{R})] \psi_+^L = E(1 + \hat{R}^\dagger \hat{R}) \psi_+^L. \quad (19)$$

The above equation corresponds to the normalized elimination of small components (NESC).^{27,52,53} For *exact* coupling \hat{R} the equation reduces to the traditional unnormalized ESC (UESC) of Eq. (6). For approximate coupling, however, NESC provides more accurate energies than UESC.^{27,53}

C. Approximate schemes

The exact coupling operator \hat{R} in its energy-dependent form (17) precludes the exact *a priori* decoupling of the Dirac Hamiltonian as well as its realization at the basis set level. Four-component basis set expansions based on “atomic balance” have been investigated by Dyall and Enevoldsen,⁵⁴ more recently by Liu and Peng,¹² and are routinely done for atomic cores in DFT calculations (see, for instance, Ref. 5). In general, however, large and small component basis functions are coupled by the nonrelativistic limit of Eq. (17),

$$\lim_{c \rightarrow \infty} c \psi^S = \frac{1}{2m} (\boldsymbol{\sigma} \cdot \mathbf{p}) \psi^L, \quad (20)$$

and this coupling is valid only for positive-energy solutions and finite nuclei.⁵⁵ The validity of this approximation can be seen in Fig. 1, where the small component radial function of the radon atom is plotted along with the radial function obtained by application of the nonrelativistic coupling [Eq. (20)] to the large component radial function. It can be seen that marked deviations occur only very close to the nucleus,

well inside the radial expectation value of the $1s_{1/2}$ orbital. Restricted kinetic balance (RKB) is the realization of Eq. (20) at the basis set level, giving a 1:1 ratio between the sizes of the large and small component basis sets. Unrestricted kinetic balance (UKB) only requires the small component basis set to span the basis functions generated by RKB. UKB generally leads to larger small component basis sets and possibly increased linear dependencies. UKB gives, on the other hand, a more flexible basis which facilitates *magnetic balance* in the calculation of magnetic properties.^{56–58} With sufficient flexibility in the basis set, the exact coupling can then be obtained during the orbital optimization procedure.⁵⁹ Figure 1 clearly shows that a basis that avoids variational collapse for an atom will also work when that atom is placed in a molecule.

Several two-component relativistic Hamiltonians are obtained using approximate couplings for which Eq. (12) is no longer valid. The Pauli Hamiltonian is obtained using

$$\hat{R} \sim \frac{1}{2mc} (\boldsymbol{\sigma} \cdot \mathbf{p}) \quad (21)$$

and retaining terms to order $O(c^{-2})$. It has no lower bound due to the mass-velocity term and furthermore contains the singular Darwin term. These difficulties are avoided in the regular approximations (RAs) based on

$$\hat{R} \sim \frac{c}{2mc^2 - V} (\boldsymbol{\sigma} \cdot \mathbf{p}), \quad (22)$$

where the potential V in the denominator is large when the momentum \mathbf{p} is large. The ZORA Hamiltonian is obtained from decoupling with Eq. (22) and no renormalization,^{18–20} that is, by the UESC approach [Eq. (6)]. Insertion of the approximate coupling [Eq. (22)] into the NESC equation [Eq. (19)] gives the IORA (infinite-order RA) equation.⁶⁰ A precursor to IORA was the scaled ZORA approach,⁶¹ which is an approximation to IORA obtained by replacing the operator product $\hat{R}^\dagger \hat{R}$ in Eq. (19) by its expectation value. Comparing the exact coupling [Eq. (17)] with the regular approximation [Eq. (22)], one sees that the latter is obtained from the former simply by setting the energy to zero. This can formally be done by setting the SS block of the metric in the Dirac equation, modified or not, to zero. UESC and NESC then gives ZORA⁶² and IORA,⁶³ respectively. ZORA and related Hamiltonians can also be derived starting from the four-component Hartree-Fock equations.⁶⁴ The Coulomb \hat{J} and exchange \hat{K} operators are then formally defined in terms of four-component orbitals, but Faas *et al.*⁶⁴ demonstrated that replacing the large components by the ZORA two-component spinors and eliminating all explicit references to small components constitute a very good approximation.

Another strategy consists of performing first the free-particle Foldy-Wouthuysen transformation,⁶⁵ which gives a two-component kinetic energy operator on a square root form, ensuring variational stability. Subsequent decoupling in orders of the external potential V or in the inverse speed of light in c^{-1} defines Douglas-Kroll-Hess^{13–15} and

Barysz-Sadlej-Snijders¹⁶ transformations, respectively. Alternatively, the small components may be eliminated and the exact coupling obtained through iterative procedures.^{66–68}

D. The one-step method

The exact coupling in the finite basis approximation can evidently be obtained by solving the Dirac equation [Eq. (2)] in some suitable basis. This sounds perhaps crazy until one realizes that this is normally not the problem one wants to solve. Rather, one seeks the approximate electronic wave function of some polyatomic molecule. The additional effort in first finding approximate solutions of the one-electron Dirac equation in a finite basis is then modest. The algorithm of Jensen and Iliáš²⁸ proceeds in two steps, basically following the program outlined by Barysz *et al.*¹⁶ and Barysz and Sadlej.^{17,22} In the first step the free-particle FW transformation is carried out. The resulting transformed Dirac equation is solved and the coupling extracted such that the exact decoupling transformation can be performed. The second step allows the construction of finite-order two-component relativistic Hamiltonians such as the first- and second-order DKH Hamiltonians.

However, whereas the first step assures variational stability and regularization of finite-order relativistic Hamiltonians, it is not required for an exact decoupling. It is therefore possible to carry out the exact decoupling in a single step starting from a matrix representation of the Dirac operator in the molecular field.

In a finite basis the coupling relations [Eq. (15)] are transformed into two systems of linear equations,

$$Y_+^S = RY_+^L, \quad Y_-^L = -R^\dagger Y_-^S, \quad (23)$$

where $Y_{+(-)}^{L(S)}$ is the block of the eigenvector matrix corresponding to the large (small) components of the positive (negative) energy solutions of the Dirac equation. The coupling R , now in matrix form, can be obtained directly by solving the first of systems of equations, but in practice it turns out to be better to take the Hermite conjugate of the second system and premultiply with Y_-^S , giving

$$AR = B, \quad A = [Y_+^S Y_-^{S\dagger}], \quad B = -[Y_-^S Y_+^{L\dagger}]. \quad (24)$$

The A matrix of this system is positive definite and Hermitian, and the system can accordingly be solved by a Cholesky decomposition. The unitary transformation can now be constructed and the Dirac Hamiltonian decoupled in matrix form.

The decoupling matrix R is used to construct the picture change transformation matrix U [Eq. (10)], which can be applied not only for the Dirac operator, but also for any four-component property operators as well. This enables carrying out easily the picture change transformation of any four-component property operator X^{4c} .

$$U^\dagger X^{4c} U \rightarrow X_{++}^{2c}. \quad (25)$$

It should be stressed, however, that the decoupling transformation U is constructed to block-diagonalize a specific Hamiltonian, defined by the external scalar potential ϕ appearing in Eq. (2). Hence, the decoupling transformation will

not in general block-diagonalize an arbitrary operator. The two-component operator X_{++}^{2c} is obtained by selecting the $(++)$ block of the transformed operator. This corresponds to projecting the four-component operator onto the space spanned by the positive-energy solutions of the particular Hamiltonian defining the decoupling transformation. It is well known that negative-energy solutions are needed in order to obtain the diamagnetic contribution from magnetic operators, at least when working with the *untransformed* Dirac-Coulomb-(Gaunt/Breit) Hamiltonian (see, however, Refs. 69 and 70). We have therefore employed the Sternheim approximation^{56,71} for the calculated magnetic properties reported in this paper; that is, we calculate the expectation value of the corresponding nonrelativistic diamagnetic operator.

Another important point is that in a rigorous construction of a two-component relativistic Hamiltonian, the decoupling transformation should be defined with respect to the complete electronic Hamiltonian [Eq. (1)], not only the one-electron part, as is usually done in the literature. The decoupling transformation would then become method dependent. Our approach allows the straightforward definition of the decoupling transformation with respect to the mean-field potential of a Hartree-Fock calculation. Such an approach, which will be computationally more expensive, could be of interest for a subsequent correlated calculation at the MP n , CI, or CC level. Evidently, not only the one-electron part, but the two-electron part as well, should be subject to the picture change transformation. However, this would bring the computational cost back to the four-component level.^{72,73} In the present publication we therefore employed the untransformed two-electron Coulomb term, which implies that two-electron spin-orbit contributions are neglected. In subsequent papers we will explore various atomic mean-field approximations to correct for this.

III. IMPLEMENTATION

In this section we describe the detailed algorithm as implemented in a development version of the DIRAC04 code.³³ Our approach is truly simple: The Dirac equation [Eq. (2)] is solved in the orthonormal [molecular orbital (MO)] basis,⁶² and the IOTC Hamiltonian with positive-energy solutions only is then projected back onto the large component atomic orbital (AO) basis. The detailed algorithm runs as follows:

- (1) Set up the Dirac equation in matrix form in the AO basis,

$$h_{c_i^{\text{AO}} c_i^{\text{AO}}}^{\text{AO}} = S^{\text{AO}} c_i^{\text{AO}} \epsilon_i, \quad S^{\text{AO}} = \begin{bmatrix} S^{LL} & 0 \\ 0 & S^{SS} \end{bmatrix}, \quad (26)$$

where S^{AO} is the overlap matrix. In our implementation we use (presently uncontracted) Gaussian basis functions and generate the small component bases by the UKB relation.⁴

- (2) Transform to the orthonormal basis using the nonunitary transformation,

TABLE I. Selected eigenstates of the Rn^{85+} one-electron system. In parentheses we report the quantity $(1-S)$ (times 10^{-4}), where S is the overlap with the renormalized large component of the corresponding four-component orbital. All values are in a.u.

	IOTC	BSS	DKH2	Scaled ZORA	ZORA
$1s_{1/2}$	-4154.662 453 0 (18.197)	453 0 (21.602)	-4142.265 045 (20.052)	-4154.779 786	-4670.480 658
$1p_{1/2}$	-1070.029 516 (0.874)	516 (0.987)	-1069.130 996 (0.806)	-1070.029 629	-1101.405 752
$1p_{3/2}$	-948.451 386 (0.813)	386 (0.881)	-948.434 642 (0.877)	-948.451 386	-973.023 298
$1d_{3/2}$	-425.136 259 (0.114)	259 (0.117)	-425.135 655 (0.117)	-425.136 259	-430.003 698
$1d_{5/2}$	-415.485 189 (0.112)	189 (0.115)	-415.485 075 (0.115)	-415.485 190	-420.132 939
$1f_{5/2}$	-234.522 726 (0.027)	726 (0.027)	-234.522 723 (0.027)	-234.522 727	-235.996 352
$1f_{7/2}$	-234.564 803 (0.026)	803 (0.027)	-232.564 801 (0.027)	-232.564 803	-234.013 854

$$h^{\text{MO}} c_i^{\text{MO}} = c_i^{\text{MO}} \varepsilon_i, \quad V = \begin{bmatrix} V^{LL} & 0 \\ 0 & V^{SS} \end{bmatrix}, \quad V^\dagger S^{\text{AO}} V = I. \quad (27)$$

In our implementation RKB is enforced in this step by embedding the transformation to Dyall's modified Dirac equation^{62,74} in the transformation V , as described in Refs. 62 and 2.

- (3) The eigenvalue problem [Eq. (27)] is solved by diagonalization, and the coupling matrix R is extracted using Eq. (24). The transformation matrix U [Eq. (10)] is constructed, and subsequently the positive-energy two-component relativistic Hamiltonian h_+^{MO} [Eq. (13)] is obtained in the matrix form. It should be noted that since the transformation to the modified Dirac equation is embedded in the orthonormalization step, the final metric will be simply the identity matrix. Thus no modification of the decoupling transformation, due to a change of metric, is necessary.
- (4) In the final step the Hamiltonian is projected back onto the large component AO basis,

$$h_+^{\text{AO}} = [V^{LL;\dagger}]^{-1} h_+^{\text{MO}} [V^{LL}]^{-1}, \quad [V^{LL}]^{-1} = V^{LL;\dagger} S^{LL;\text{AO}}.$$

The matrix representation of the IOTC Hamiltonian, h_+^{AO} , is then written to file with whatever transformed property operators are needed, and all the subsequent calculations continue in the two-component mode.

Compared to the scheme proposed by Jensen and Iliaš,²⁸ the preliminary free-particle FW transformation is completely avoided. Since this transformation was used by Barysz *et al.*,¹⁶ we will refer to the two-step approach as BSS. The direct construction of the coupling matrix advocated here was already proposed by Dyall⁵³ as well as by Liu and Peng¹² and Kutzelnigg and Liu,³⁰ although the latter authors seem to favor an iterative approach. A particular aspect of this work is that we work in an orthonormal kinetically balanced basis and thus the *renormalized* modified Dirac equation, which simplifies operations and allows control of

linear dependencies. The quaternion symmetry scheme^{9,62} employed in DIRAC furthermore allows a straightforward separation of scalar and spin-orbit terms. This will be explored in a subsequent publication.

As already mentioned in Sec. II, it is also possible to perform the decoupling transformation with respect to a (converged) four-component Fock operator. Then one iteration in the subsequent two-component HF-SCF cycle reproduces exactly the total HF-SCF energy and orbital energies of the four-component calculation.

IV. COMPUTATIONAL DETAILS

The IOTC Hamiltonian as well as the BSS, DKH, and ZORA Hamiltonians are all implemented in the DIRAC program,³³ which allows direct comparison, also with calculations based on the four-component Dirac-Coulomb Hamiltonian. We have tested the performance of the IOTC Hamiltonian by calculations on the radon atom. We have used Dyall's triple-zeta basis $30s26p17d11f$ (Ref. 75) in uncontracted form since contraction is yet to be implemented for our two-component approach. The nuclear charge distribution was modeled by a Gaussian distribution.⁷⁶

Fock-space coupled cluster (FSCCD) calculations⁴⁰ were done with $5d^{10}6s^26p^6$ correlated electrons, and $6s^26p^6$ shells were added to the active space [the (1,0) sector]. Virtual spinors with energies higher than 1000 a.u. were deleted.

The static electric dipole polarizability, magnetizability, and NMR shielding were calculated as linear response functions⁴⁴ based on the HF wave function. The ratios of norms between residual and solution vectors of the linear response equation were converged to 1.0×10^{-9} . For magnetic properties we kept the rotations between positive-energy orbitals, while the diamagnetic terms were calculated as an expectation value using the corresponding nonrelativistic diamagnetic operator.^{56,77}

TABLE II. Total HF and selected orbital energies of the neutral Rn atom. On the second line of each entry we report the relative error (in %) with respect to the benchmark DC values as well as the quantity $(1-S)$ (times 10^{-4}), where S is the overlap with the renormalized large component of the corresponding four-component orbital; the latter quantity is in parentheses. For ZORA results (2c) and (4c) refer to results using two or four spinors, respectively. The mean absolute error (MAE) is indicated for the complete set of occupied orbitals. It is also indicated separately for the SR orbital energies, obtained as the weighted average of spin-orbit components, and the SO splittings.

	DC	IOTC	BSS	DKH2	Scaled ZORA(4c)	Scaled ZORA(2c)	ZORA(4c)	ZORA(2c)
SCF energy	-23 602.103 650	-23 593.210 805	-23 592.127 595	-23 561.975 759	-23 601.711 805	-24 764.526 289	-23 601.711 805	-24 764.526 289
		0.038	0.042	0.170	0.002	-4.925	0.002	-4.925
$1s_{1/2}$	-3641.197 128	-3635.591 512 0.154 (17.565)	-3634.923 280 0.172 (20.858)	-3622.999 193 0.500 (19.343)	-3634.674 542 0.179	-3632.202 432 0.247	-4079.593 966 12.040	-4076.454 181 11.954
$3s_{1/2}$	-166.833 033	-166.637 744 0.117 (0.147)	-166.628 842 0.122 (0.147)	-166.328 607 0.302 (0.150)	-166.552 452 0.168	-166.545 427 0.172	-168.000 680 0.700	-167.997 062 0.698
$6s_{1/2}$	-1.071 416	-1.070 457 0.090 (0.020)	-1.070 439 0.091 (0.021)	-1.067 887 0.329 (0.075)	-1.071 252 0.015	-1.069 457 0.183	-1.071 416 0.000	-1.069 621 0.168
$2p_{1/2}$	-642.329 988	-643.996 448 -0.259 (0.944)	-643.900 000 -0.244 (1.028)	-643.235 249 -0.141 (0.854)	-640.266 300 0.321	-641.772 371 0.087	-656.971 260 -2.279	-658.560 461 -2.527
$2p_{3/2}$	-541.102 218	-539.854 596 0.231 (0.538)	-539.804 784 0.240 (0.528)	-539.863 182 0.229 (0.585)	-539.609 004 0.276	-540.577 464 0.097	-551.780 913 -1.974	-552.795 587 -2.161
$6p_{1/2}$	-0.540 307	-0.544 087 -0.700 (0.094)	-0.544 022 -0.688 (0.090)	-0.543 170 -0.530 (0.043)	-0.539 367 0.174	-0.540 330 -0.004	-0.539 427 0.163	-0.540 390 -0.015
$6p_{3/2}$	-0.383 987	-0.382 766 0.318 (0.035)	-0.382 761 0.319 (0.036)	-0.383 233 0.196 (0.026)	-0.383 759 0.059	-0.383 983 0.001	-0.383 790 0.051	-0.384 015 -0.007
$5d_{3/2}$	-2.189 578	-2.208 340 -0.857 (0.012)	-2.208 468 -0.863 (0.012)	-2.210 278 -0.945 (0.014)	-2.187 899 0.077	-2.191 355 -0.081	-2.188 933 0.029	-2.192 393 -0.129
$5d_{5/2}$	-2.016 466	-2.006 421 0.498 (0.006)	-2.006 559 0.491 (0.006)	-2.008 268 0.407 (0.005)	-2.015 487 0.049	-2.017 081 -0.030	-2.016 384 0.004	-2.017 980 -0.075
$4f_{5/2}$	-9.193 822	-9.275 596 -0.889 (0.009)	-9.276 245 -0.897 (0.009)	-9.280 862 -0.947 (0.010)	-9.189 778 0.044	-9.200 166 -0.069	-9.207 223 -0.146	-9.217 667 -0.259
$4f_{7/2}$	-8.928 117	-8.875 701 0.587 (0.002)	-8.875 701 0.587 (0.002)	-8.876 344 0.580 (0.002)	-8.925 095 0.034	-8.930 453 -0.026	-8.941 694 -0.152	-8.947 090 -0.213
MAE (total)		0.234	0.261	0.758	0.272	0.375	18.267	18.136
MAE (SR/SO)		0.473/0.543	0.528/0.537	1.455/0.431	0.705/0.085	0.759/0.008	31.271/0.468	31.180/0.557

V. RESULTS AND DISCUSSION

We first consider the one-electron system Rn^{85+} . In Table I we present results for selected orbitals using the one-step IOTC and two-step BSS Hamiltonians. The eigenvalues are by construction strictly identical to the original Dirac operator. However, when we calculate the overlap of eigenvectors with the corresponding renormalized Dirac large components, small differences appear, indicating that the eigenvectors are not identical. The IOTC and BSS transformation matrices are different, and this will have consequences for energies in many-electron calculations as well due to the lack of picture change transformation for the two-electron operator. We have also compared these results with lower-order two-component Hamiltonians—DKH2 (Ref. 28) and (scaled) ZORA (Ref. 62)—calculated with the same code and basis sets. More pronounced discrepancies now appear, in particular, for the inner orbitals. The greater precision of the scaled ZORA compared to normal ZORA is particularly striking.

In Table II we present results of HF calculations of the ground state of the neutral radon atom. IOTC and BSS orbital energies now differ from each other and from the four-component results due to the lack of picture change transfor-

mation of the Coulomb term: The mean absolute errors (MAEs) in energies of the complete set of occupied orbitals are 0.234 and 0.261 a.u. These deviations are clearly smaller than the results obtained with the DKH2 Hamiltonian for which a MAE of 0.758 a.u. is observed. Scaled ZORA shows, on the other hand, deviations closer to the IOTC results, although a slight degradation is observed when constructing the mean-field potential from ZORA two-spinors (MAE of 0.375 a.u.) rather than four-spinors (MAE of 0.272 a.u.). Normal ZORA is clearly not satisfying. These observations can be sharpened by looking at the mean absolute errors of spin-orbit (SO) splittings and spin-free (SR) orbital energies separately, the latter obtained as the weighted average of spin-orbit components: The scaled ZORA spin-free orbital energies are clearly less accurate than the IOTC ones, but the Dirac-Coulomb (DC) spin-orbit splittings are significantly better reproduced by the scaled ZORA calculations than by using the IOTC/BSS Hamiltonians, since the former Hamiltonian incorporates spin-orbit corrections to the two-electron interaction. For normal ZORA the difference in accuracy between spin-free and spin-orbit values is particularly noteworthy.

TABLE III. IEs of the Rn atom and EEs of the Rn⁺ cation (in eV). Absolute differences from DC values in parentheses.

	DC	IOTC	BSS	DKH2
IE ^a				
¹ S ₀ - ² P _{3/2}	10.5614	10.5304 (-0.0310)	10.5304 (-0.0310)	10.5410 (-0.0204)
EE of Rn ⁺				
² P _{3/2} - ² P _{1/2}	3.7706	3.8967 (0.1261)	3.8953 (0.1247)	3.8644 (0.0938)
² P _{3/2} - ² S _{1/2}	14.8708	14.8427 (-0.0281)	14.8420 (-0.0288)	14.8279 (-0.0429)

^aThe experimental value of the first IE (¹S₀-²P_{3/2}) is 10.7485 eV (Ref. 81).

Table III contains spectroscopic properties—ionization energy (IE) of the Rn atom as well as excitation energy (EE) of its cation—calculated at the FSCSD level. The two-component results agree well with the four-component Dirac-Coulomb values. One may note that the DKH2 Hamiltonian can compete with the infinite-order Hamiltonians for these valence properties. A fair comparison with experiment would, on the other hand, require a larger basis set, a larger active space, and more advanced Fock-space coupled cluster approaches.⁷⁸

NMR shielding constants, magnetizabilities, and polarizabilities calculated using DC, BSS, and IOTC Hamiltonians are collected in Table IV. We do not report DKH2 or ZORA data since we have not implemented picture change transformation of property operators for these finite-order Hamiltonians. For magnetic properties we indicate separately the paramagnetic and diamagnetic parts. It should be noted that the nonrelativistic paramagnetic contributions are strictly zero for closed-shell atoms since the magnetic dipole operator appearing in the corresponding linear response functions is proportional to the orbital angular momentum operator. Again, IOTC and BSS results match with each other, and both follow closely four-component values. Our results obtained for the NMR shielding is furthermore in excellent agreement with the four-component calculations reported by

TABLE IV. Magnetic and electric properties of the Rn atom. Absolute differences from DC values are in parentheses.

	DC	IOTC	BSS
NMR shielding ^a			
Total	23 348.4	23 373.6 (25.2)	23 372.4 (24.0)
Diamagnetic	12 412.2	12 405.2 (-7.0)	12 404.3 (-7.9)
Paramagnetic	10 936.2	10 968.4 (32.2)	10 968.0 (31.8)
Magnetizability ^b			
Total	-12.7160	-12.7230 (-0.0070)	-12.7236 (-0.0076)
Diamagnetic	-12.7460	-12.7550 (-0.0090)	-12.7556 (-0.0096)
Paramagnetic	0.0299	0.0320 (0.0021)	0.0319 (0.0020)
Polarizability ^b			
	27.066	27.119 (0.053)	27.122 (0.056)

^aNMR shielding constants in ppm.

^bMagnetizabilities in a.u.

^cPolarizabilities in a.u.

Vaara and Pyykkö,⁷⁹ they obtained 12 410 and 23 350 ppm for the diamagnetic term and the total shielding constant, respectively.

VI. CONCLUSION

In this paper we have reported the implementation and application of the one-step approach to the generation of the infinite-order two-component relativistic Hamiltonian, based entirely on matrix algebra. Due to its simplicity, it should be preferred to the two-step procedure of Jensen and Iliaš.²⁸ Our test calculations even suggest a slightly better performance of the IOTC Hamiltonian.

At this point it is natural to ask what has been achieved. Compared to four-component calculations, our IOTC Hamiltonian is expected to give significant speedups, on the order of 10 or better and independent of system size, at the HF, DFT, and MP2 levels. Liu and Peng¹² have reported identical costs for two- and four-component calculations using local density approximation/generalized gradient approximation functionals, but it remains to be demonstrated whether their approach can be generalized to hybrid functionals as well as HF and MP2 calculations. On the other hand, there will be no computational savings at the CC and CI levels.² Furthermore, the infinite-order one-electron Hamiltonian should be supplemented by picture change corrections to the two-electron part. This can probably be achieved by an atomic/fragment mean-field approach⁸⁰ which should preferably be extensible to response calculations. A possible bottleneck in the calculations based on the IOTC Hamiltonian will be the size of the matrix representation of the Dirac operator. This can probably be circumvented by constructing the decoupling transformation from atomic or, more generally, fragment calculations, as already suggested by Liu and Peng.¹²

A final point is that two-component approaches tend to lack the simplicity and transparency of four-component operators. As already pointed out by Foldy and Wouthuysen,⁶⁵ four-component operators refer to the instantaneous position of electrons whereas two-component ones refer to a *mean* position upon which is superimposed the *Zitterbewegung* of the electron. This leads to the explicit introduction of Darwin and spin-orbit terms in two-component Hamiltonians.

The IOTC (and XQR) Hamiltonian is expected to outperform existing finite-order Hamiltonians based on the regular approximation (i.e., ZORA) or DKH/BSS transformation, but this will strongly depend on the computational implementation as well. The former Hamiltonians completely avoid the complexity of generating operator expressions for higher-order contributions or picture changed property operators. Further testing and development, the generation of analytic molecular gradients in particular, is required, but there is no doubt that the introduction of infinite-order two-component relativistic Hamiltonians by matrix algebra has opened up new and exciting perspectives in relativistic quantum chemistry.

ACKNOWLEDGMENTS

The authors thank the French Ministry of Science and Technology for funding the postdoctoral position of one of

the authors (M.I.) in Strasbourg. M.I. gratefully acknowledges further financial support from the Slovak Grant Agency (Contract No. 1/3560/06). This work was supported by the Slovak Research and Development Agency under Contract No. APVV-20-018405. Last but not the least, the authors would also like to thank H. J. Aa. Jensen (Odense) for stimulating discussions.

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