

## Chapter 11

# Two-component methods and the generalised Douglas–Kroll transformation

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## Abstract

In this chapter the reduction of relativistic quantum chemistry to two-component form is discussed. Since the charge-conjugated degrees of freedom are of negligible importance for chemical purposes, the computational cost for relativistic quantum chemical calculations may significantly be reduced by their elimination. This transition to two-component formulations may either be achieved by elimination techniques for the small component or by suitably chosen unitary transformations which decouple the Hamiltonian. Amongst the latter, the Douglas–Kroll transformation is a very successful and well-established procedure. Its central idea is the expansion of the Hamiltonian in even terms of definite order in the external potential, achieved by the application of a sequence of unitary transformations, which eliminate the odd terms of the Hamiltonian step by step. We discuss the most general form of the parametrisation of these unitary transformations and derive the DK approximations up to fourth order. All resulting DK Hamiltonians turn out to be independent of the chosen parametrisation of the unitary matrices. The accuracy of the third- and fourth-order Hamiltonians  $H_{\text{DKH3}}$  and  $H_{\text{DKH4}}$  is investigated.

## 1. INTRODUCTION

During the second half of the last century chemistry revealed a large number of systems, whose theoretical description requires an extension of the framework of non-relativistic quantum mechanics. For example, the spectral properties and binding energies of heavy element compounds and transition-metal complexes are governed by relativistic effects. Many experimental results for

these quantities are far off the non-relativistic predictions resulting from the Schrödinger equation. Detailed discussions of the importance of relativistic effects in chemistry were given by Pekka Pyykkö [1–3], who was one of the first to realise the importance of relativity for chemical systems. He also contributed three volumes with an exhaustive overview over the literature of this field [4–6], which are also available online on the world-wide web [7].

Those intrinsically relativistic systems require the framework of relativistic quantum chemistry, which is based on the Dirac equation. Its position-space representation for a single electron in the attractive Coulomb potential of a nucleus with charge  $Z$  reads

$$H_D \phi(\mathbf{r}) = [c \boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1) mc^2 + V(\mathbf{r})] \phi(\mathbf{r}) = E \phi(\mathbf{r}), \quad (1)$$

where  $V(\mathbf{r})$  is the external potential of Coulomb type,  $V(\mathbf{r}) = -Ze^2/r$ , or alternatively a potential derived from an extended nuclear charge distribution. In order to get electronic binding energies comparable to the non-relativistic theory the energy scale is shifted by the rest energy  $mc^2$  of the electron. The Dirac spinor is a four-component quantity,

$$\phi(\mathbf{r}) = \begin{pmatrix} \phi^L(\mathbf{r}) \\ \phi^S(\mathbf{r}) \end{pmatrix}, \quad (2)$$

where the the upper and lower two components  $\phi^L$  and  $\phi^S$  are Pauli 2-spinors originating from the electronic and positronic degrees of freedom. For solutions with positive energy and weak potentials the latter is suppressed by a factor of  $(2mc)^{-1}$  with respect to the former, and thus commonly dubbed small component  $\phi^S$  as opposed to the large component  $\phi^L$ . Taking advantage of the structure of the four Dirac matrices

$$\boldsymbol{\alpha} = \begin{pmatrix} 0 & \boldsymbol{\sigma} \\ \boldsymbol{\sigma} & 0 \end{pmatrix}, \quad \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (3)$$

with

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad (4)$$

being the familiar Pauli matrices, Eq. (1) can be given in ‘split notation’ as

$$(V - E) \phi^L + c \boldsymbol{\sigma} \cdot \mathbf{p} \phi^S = 0, \quad (5)$$

$$c \boldsymbol{\sigma} \cdot \mathbf{p} \phi^L + (V - 2mc^2 - E) \phi^S = 0, \quad (6)$$

where the coupling between the large and small components via the odd (off-diagonal) operator  $c \boldsymbol{\alpha} \cdot \mathbf{p}$  is manifest. By contrast, even (block-diagonal) operators like  $\beta$  or  $V$  do not cause any coupling between  $\phi^L$  and  $\phi^S$ .

It should be mentioned that the coupling between the four components of a Dirac spinor is accomplished by the mathematical structure of a four-dimensional Clifford algebra, i.e., the Dirac equation is completely determined by the postulate that the four Dirac matrices shall satisfy the fundamental anti-commutation relation

$$\{\gamma^\mu, \gamma^\nu\} = 2g^{\mu\nu}. \quad (7)$$

This requirement does not fix the Dirac matrices uniquely, and thus the whole Dirac theory and all systematic approximations to it could equally well be formulated in terms of general four-dimensional quaternions, which are independent of a special representation and rely only on the algebraic properties of the Clifford algebra [8–10]. Such an implementation of the Dirac theory is known to speed up diagonalisation procedures significantly, and has successfully been employed in modern four-component relativistic program packages like DIRAC [11]. However, the salient features of this approach can hardly be transferred to two-component methods, and we therefore focus in our presentation in the following only on the common ‘standard representation’ of the Dirac algebra given above.

The spectrum of the single-electron Dirac operator  $H_D$  and its eigenspinors  $\phi$  for Coulombic potentials are known in analytical form since the early days of relativistic quantum mechanics. However, this is no longer true for a many-electron system like an atom or a molecule being described by a many-particle Hamiltonian  $H$ , which is the sum of one-electron Dirac Hamiltonians of the above kind and suitably chosen interaction terms. One of the simplest choices for the electron interaction yields the Dirac–Coulomb–Breit (DCB) Hamiltonian, where only the frequency-independent first-order correction to the instantaneous Coulomb interaction is included,

$$H = \sum_{i=1}^n H_D(i) + \sum_{i<j} g_{ij} \quad (8)$$

with

$$g_{ij} = \frac{e^2}{r_{ij}} + B_{ij} = \frac{e^2}{r_{ij}} - \frac{e^2}{2r_{ij}} \left( \boldsymbol{\alpha}_i \cdot \boldsymbol{\alpha}_j + \frac{(\boldsymbol{\alpha}_i \cdot \mathbf{r}_{ij})(\boldsymbol{\alpha}_j \cdot \mathbf{r}_{ij})}{r_{ij}^2} \right). \quad (9)$$

Closed-form solutions for orbital equations derived with this Hamiltonian are far out of reach, and numerical methods have to be employed. While theoretically most appealing, those four-component methods are computationally very expensive due to the fact that the charge-conjugated degrees of freedom are treated as dynamical variables. However, in most situations of chemical interest the threshold for pair-creation processes and excitations of the positronic degrees of freedom is far beyond the energy of the valence shell, and it is thus a very good approximation to integrate them out at the very beginning. This can either be achieved by elimination techniques for the small component or by appropriately chosen unitary transformations, which annihilate the coupling between the electronic and positronic degrees of freedom, i.e., which remove the odd terms in the Hamiltonian. The latter result in decoupled transformed Hamiltonians, which do still act on wavefunctions being based on four-component spinors, but where we now have the possibility to focus on the positive energy part of these spinors and work with two-component objects only.

For both the elimination and transformation techniques the momentum-space representation of the Dirac equation,

$$H_D \phi(\mathbf{p}) = [c \boldsymbol{\alpha} \cdot \mathbf{p} + (\beta - 1) mc^2 + V] \phi(\mathbf{p}) = E \phi(\mathbf{p}) \quad (10)$$

may be convenient, which is obtained by a Fourier transformation of Eq. (1). Here the external potential is no longer a local (multiplicative) operator, but acts as an integral operator

$$V \phi(\mathbf{p}) = \int \frac{d^3 \mathbf{p}'}{(2\pi\hbar)^3} V(\mathbf{p} - \mathbf{p}') \phi(\mathbf{p}') \quad (11)$$

on the spinor  $\phi$ . The kernel of  $V$  is the Fourier transform of  $V(\mathbf{r})$ , i.e.,

$$V(\mathbf{p} - \mathbf{p}') = \int d^3 r \exp\left[-\frac{i}{\hbar} (\mathbf{p} - \mathbf{p}') \cdot \mathbf{r}\right] V(\mathbf{r}) = -\frac{4\pi Z e^2 \hbar^2}{|\mathbf{p} - \mathbf{p}'|^2} \quad (12)$$

for a Coulomb potential  $V(\mathbf{r}) = -Ze^2/r$ . Thus, the four coupled differential equations (1) were transformed into four coupled integral equations (10), which are often a more convenient starting point for approximations, especially if the operators are represented in a basis of single particle wave functions.

In the following overview, the theory of two-component methods in relativistic quantum chemistry is shortly reviewed. The relationship between the large and small component is analysed in section 2, followed by a discussion of possible methods to decouple the Dirac Hamiltonian. The focus is equally distributed

on both elimination and transformation techniques, with special emphasis on the discussion of their validity, accuracy, and computational cost. Special attention will be paid to the Douglas–Kroll (DK) method, which is discussed comprehensively in section 3, where the underlying assumptions and approximations are studied in detail, and new insight into the structure of the DK transformation is gained. First, an extension of the parametrisation of the employed unitary transformations is introduced by an general power series expansion in an antihermitean matrix. Afterwards it is shown that the even terms in the DK Hamiltonian up to fourth order in the external potential do not depend on the choice of this parametrisation. This section ends with a detailed presentation of technical aspects to be considered by an implementation of the DK method into existing computer codes. In section 4 the first numerical results obtained with this fourth order Douglas–Kroll Hamiltonian (DKH4) are given, and the binding energies of hydrogenlike atoms for the whole periodic table are compared to the exact values obtained from the Dirac equation. Furthermore, all-electron SCF calculations with DKH4 for noble gas atomic systems up to element 118 (Eka-Rn) are presented and compared to the numerical four-component Dirac–Fock benchmark results. In section 5 the problem of the transformation of the wavefunction to two-component form is discussed, with special focus on the so-called ‘picture change effect’, which has amply been discussed in the recent literature. Our presentation closes with conclusions and further perspectives for the field of two-component methods in quantum chemistry.

## 2. METHODS TO DECOUPLE THE DIRAC EQUATION

### 2.1. Relationship between the large and small components

In this section different methods to decouple the Dirac equation are discussed. A useful prerequisite for this reduction to two-component form is the analysis of the relationship between the large and small components of an exact eigen-solution of the Dirac equation. For every Dirac 4-spinor  $\phi$  given by equation (2), which has not necessarily to be an eigenspinor of  $H_D$ , this relationship may be formalised by

$$\phi^S = X\phi^L, \quad (13)$$

where  $X$  is a yet undetermined  $(2 \times 2)$ -matrix operator, whose properties are the subject of investigation in this subsection.

If and only if  $\phi$  is an exact solution of the Dirac equation (1), an apparently simple expression for  $X$  can immediately be given in closed form by employing

Eq. (6),

$$X = X(E) = (E - V + 2mc^2)^{-1} c \boldsymbol{\sigma} \cdot \mathbf{p}. \quad (14)$$

However, there is a serious problem connected with this energy-dependent expression for  $X$ , which will be fully illuminated only by the subsequent consideration of its energy-independent formulation given below. As  $E$  decreases towards the positronic continuum, the inverse operator on the right hand side will inevitably cross its singularity at  $E = V - 2mc^2$ . As a consequence, one unique and universal  $X$ -operator valid for the whole energy range describing both electronic and positronic solutions does not exist. Nevertheless, a direct substitution of  $\phi^S = X\phi^L$  into Eq. (5) yields a two-component equation for the large component only, which will be discussed in the next subsection. The explicit energy dependence of the operator  $X$  is undesirable, however, since it gives rise to non-hermitean operators and non-orthogonal orbitals.

In order to arrive at an energy-independent expression for  $X$ , it is necessary to utilise the Dirac equation in a more sophisticated fashion. By multiplication of Eq. (5) with  $X$  from the left and taking advantage of Eqs. (6) and (13) we arrive at

$$XV\phi^L + Xc\boldsymbol{\sigma} \cdot \mathbf{p}X\phi^L = c\boldsymbol{\sigma} \cdot \mathbf{p}\phi^L + VX\phi^L - 2mc^2X\phi^L. \quad (15)$$

The operator  $X$  has to satisfy this equation for all possible choices for the large component  $\phi^L$ , and is thus determined by the non-linear operator identity

$$X = \frac{1}{2mc^2} \{ c\boldsymbol{\sigma} \cdot \mathbf{p} - [X, V] - Xc\boldsymbol{\sigma} \cdot \mathbf{p}X \}. \quad (16)$$

The solution of this equation is as complex as the solution of the Dirac equation itself, and thus only for a restricted class of potentials closed-form solutions for  $X$  are known [12].

It is important to realise that Eq. (16) is a quadratic equation for  $X$  and has thus always two independent solutions  $X_+$  and  $X_-$ , corresponding to electronic ( $E > -mc^2$ ) and positronic ( $E < -mc^2$ ) spinors, respectively. They originate only due to the fact that the Dirac equation describes both electrons and positrons on equal footing. As in the case of very strong potentials even electronic solutions may have energies below  $-2mc^2$  within the positronic continuum, it was suggested to refer to all solutions corresponding to  $X_+$  more rigorously as *class I* solutions by Heully and co-workers [13]. Accordingly all solutions connected to  $X_-$  are called *class II* solutions.

In order to demonstrate the ambiguity of the  $X$ -operator, explicit expressions for both  $X_+$  and  $X_-$  are given for the case of a free particle, defined by  $V = 0$ ,

$$X_{\pm}^{V=0} = (E_{\pm} + mc^2)^{-1} c \boldsymbol{\sigma} \cdot \mathbf{p}, \quad (17)$$

where

$$E_{\pm} = E_{\pm}(\mathbf{p}) = \pm E_p, \quad E_p = \sqrt{\mathbf{p}^2 c^2 + m^2 c^4} > 0 \quad (18)$$

is the familiar square root operator reflecting the relativistic energy-momentum relation. We note in passing that  $X_+^{V=0}$  defines the exact free-particle Foldy-Wouthuysen (fpFW) transformation to be discussed in detail later on. The action of the operator  $X$  is most conveniently studied in momentum space, where the inverse operator may be applied in closed form without expanding the square root. Thus the four normalised free-particle Dirac eigenspinors with the eigenvalues  $E_{\pm} - mc^2$  can compactly be given as ( $s = 1, 2$ )

$$\phi_{\pm,s}(\mathbf{p}, t) = \underbrace{\sqrt{\frac{E_{\pm} + mc^2}{2E_{\pm}}} \begin{pmatrix} \chi_s \\ X_{\pm}^{V=0} \chi_s \end{pmatrix}}_{u_{\pm,s}(\mathbf{p})} \exp \left[ \frac{i}{\hbar} (\mathbf{p} \cdot \mathbf{r} - E_{\pm} t) \right] \quad (19)$$

with

$$\chi_1 = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \quad \chi_2 = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \quad (20)$$

We have chosen the standard convention of quantum chemistry and have normalised the spinors to unity instead of to  $E_p/mc^2$ , which can often be found in the physics literature. After some elementary algebraic manipulations the standard form of the spinors  $u_{\pm}$  is obtained as

$$u_{+,s} = \begin{pmatrix} \sqrt{\frac{E_p + mc^2}{2E_p}} \chi_s \\ \frac{c \boldsymbol{\sigma} \cdot \mathbf{p}}{\sqrt{2E_p(E_p + mc^2)}} \chi_s \end{pmatrix}, \quad u_{-,s} = \begin{pmatrix} \frac{c \boldsymbol{\sigma} \cdot \mathbf{p}}{\sqrt{2E_p(E_p + mc^2)}} \chi_s \\ -\sqrt{\frac{E_p + mc^2}{2E_p}} \chi_s \end{pmatrix}. \quad (21)$$

In the literature the relation  $\phi^S = X\phi^L$  with  $X$  defined by Eq. (16) is sometimes called *exact kinetic balance*. According to the derivation of Eq. (16) kinetic balance is always guaranteed exactly for strict eigensolutions of the Dirac

equation. Recently, another important consequence of the fulfilment of exact kinetic balance was realised by Kutzelnigg [14]. As long as exact kinetic balance is guaranteed for all Dirac spinors under consideration, i.e., all spinors within the space of testfunctions  $\mathcal{H}_{\text{var}}$ , a *variational* scheme is established. Variational means, that the energy expectation value  $\langle H_D \rangle_\phi$  is bounded from below by the exact electronic ground state energy  $E_0$ ,

$$\langle H_D \rangle_\phi = \langle \phi | H_D | \phi \rangle \leq E_0, \quad \forall \phi \in \mathcal{H}_{\text{var}}. \quad (22)$$

If the relation  $\phi^S = X\phi^L$  is, however, only satisfied approximately for at least some Dirac spinors under consideration, only a *variationally stable* approach is achieved. I.e., the energy expectation value is still bounded from below, but not necessarily by  $E_0$ , but by a different bound which may be above or below  $E_0$ .

The various two-component theories known from the literature satisfy the kinetic balance relation only to certain degrees of accuracy and hence establish only variationally stable but not variational approaches. The simplest approximation to exact kinetic balance may be obtained in the non-relativistic limit of Eqs. (14) or (16),

$$X_+ \xrightarrow{c \rightarrow \infty} \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc}, \quad X_- \xrightarrow{c \rightarrow \infty} -2mc (\boldsymbol{\sigma} \cdot \mathbf{p})^{-1}. \quad (23)$$

The introduction of the operator  $X$  leads to a modified normalisation description for the Dirac spinor  $\phi$ ,

$$\langle \phi | \phi \rangle = \langle \phi^L | \phi^L \rangle + \langle \phi^S | \phi^S \rangle = \langle \phi^L | 1 + X^\dagger X | \phi^L \rangle \stackrel{!}{=} 1, \quad (24)$$

which can now be expressed in terms of the large component only, and has to be taken into account when dealing with a two-component theory.

We conclude this section by mentioning that the relationship between the large and small components presented above could equally well be formulated in terms of an operator  $Y$  defined by

$$\phi^L = Y\phi^S. \quad (25)$$

The  $X$ - and  $Y$ -operators are, of course, closely related to each other, and apart from the trivial equality  $X_\pm = Y_\pm^{-1}$  they satisfy always the condition  $X_\pm = -Y_\mp^\dagger$ . A comprehensive discussion of this connection can be found in Ref. [13]. In the remainder of this article we will only deal with class I (electronic) solutions and thus introduce the abbreviations  $X := X_+$  and  $Y := Y_- = -X^\dagger$ .



## 2.2. Elimination of the small component

The central idea of all elimination methods for the small component is to employ relations (13) and (14) and to substitute  $\phi^S$  in Eq. (5) by an expression for the large component only. This yields a two-component equation for the latter only, which can be written as

$$(V - E) \phi^L + \frac{1}{2mc^2} [(c \boldsymbol{\sigma} \cdot \mathbf{p}) \omega (c \boldsymbol{\sigma} \cdot \mathbf{p})] \phi^L = 0, \quad (26)$$

with

$$\omega = \left[ 1 - \frac{V - E}{2mc^2} \right]^{-1} = \sum_{k=0}^{\infty} \left( \frac{V - E}{2mc^2} \right)^k, \quad (27)$$

where we have utilised the properties of the geometric series in the second step of Eq. (27). Note that the non-relativistic Schrödinger equation is recovered by restricting this expansion to zeroth order, i.e., setting  $\omega = 1$ .

The historically first reduction of the Dirac equation to two-component form is the Pauli approximation, which can be obtained from Eq. (26) by truncating the series expansion for  $\omega$  after the first two terms, and eliminating the energy dependence by means of a systematic expansion in  $c^{-2}$ . The result is the familiar Pauli Hamiltonian

$$H_{\text{Pauli}} = \frac{\mathbf{p}^2}{2m} + V - \frac{p^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}(\Delta V) + \frac{\hbar}{4m^2c^2} \boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}], \quad (28)$$

where the mass-velocity term  $-p^4/8m^3c^2$ , the Darwin term  $\hbar^2 \Delta V/8m^2c^2$ , and the spin-orbit coupling term proportional to  $\boldsymbol{\sigma} \cdot [(\nabla V) \times \mathbf{p}]$  describe relativistic corrections correct up to  $O(c^{-2})$ . However, several problems are connected with the Pauli Hamiltonian and prohibit its use within a variational procedure. First the minus sign of the mass-velocity term yields a strongly attractive potential for states with high momentum, and would thus lead to variational collapse, since it is not bounded from below. The Darwin term degenerates to a highly singular Delta distribution term if a point-like nucleus is applied, and the spin-orbit coupling term is not bounded from below either. These insurmountable problems cannot be remedied by going to higher orders [15], since the expansion of  $\omega$  is only valid for  $|V - E| < 2mc^2$ , which is certainly violated in regions close to the nucleus. Therefore the Pauli Hamiltonian and all other operators based on simple expansions of  $\omega$  in powers of  $c^{-2}$  are in general singular and may not be used for variational procedures. They are applicable only within perturbation theory to lowest order. The Pauli Hamiltonian yields satisfactory

relativistic corrections to the energy up to the first and second transition metal row.

Since  $\omega$  is a scalar operator, even this simple energy-dependent elimination of the small component permits an exact separation of the spin-free and spin-dependent terms of the Dirac Hamiltonian by applying Dirac's relation

$$(\boldsymbol{\sigma} \cdot \mathbf{p}) \omega (\boldsymbol{\sigma} \cdot \mathbf{p}) = \mathbf{p} \cdot \omega \mathbf{p} + i \boldsymbol{\sigma} \cdot (\mathbf{p} \times \omega \mathbf{p}) \quad (29)$$

to the two-component operator of Eq. (26). This is still valid in an improved version of the original Pauli approximation, where the small component was eliminated in an exact way by avoiding any truncation of the expansion (27) [16–23]. Then, equation (26) reproduces exactly both the positive and negative eigenvalues of the Dirac Hamiltonian, and has been successfully applied in atomic many-body calculations [24,25]. However, all operators of this kind are non-hermitean and energy-dependent and thus plagued by not mutually orthogonal orbitals.

In the mid-eighties another method to eliminate the small component has been developed in order to arrive at regular expansions for the Hamiltonian [13,26]. These regular approximations are based on the general theory of effective Hamiltonians [27,28], where the full problem under consideration is projected onto a smaller, suitably chosen model space with an effective Hamiltonian, which comprises all desired properties of the problem sufficiently well. In the case of the Dirac Hamiltonian the basic idea, being as simple as ingenious, is to rewrite the expression for  $\omega$  in the form

$$\omega = \frac{2mc^2}{2mc^2 - V} \left[ 1 + \frac{E}{2mc^2 - V} \right]^{-1}, \quad (30)$$

and to choose the new expansion parameter  $E/(2mc^2 - V)$ , which is the starting point for the so-called regular approximations developed by the Amsterdam group [29–31] to a workable and successful method of electronic structure theory. A truncation of this expansion for  $\omega$  defines the zero- and first-order regular approximation (ZORA, FORA) [32]. A particular noteworthy feature of ZORA is that even in this zeroth order approximation there is an efficient relativistic correction for the region close to the nucleus, where the main relativistic effects come from. Excellent agreement of orbital energies and other valence shell properties with the results from the Dirac equation is obtained, and can even be improved by transition to the *scaled* ZORA variant [33], which takes the renormalisation to the transformed large component approximately into ac-

count, using

$$\frac{1}{\sqrt{1 + X^\dagger X}} \phi_i^L \approx \frac{1}{\sqrt{1 + \langle \phi_i^L | X^\dagger X | \phi_i^L \rangle}} \phi_i^L. \quad (31)$$

The analysis [34] shows that in regions of high potential the ZORA Hamiltonian reproduces relativistic energies up to an error of order  $-E^2/c^2$ . On the other hand, in regions of small potential but high kinetic energy of the particle, it does not provide any relativistic correction. The main disadvantage of the method is its gauge dependence, i.e., a constant shift of the electrostatic potential does not lead to a constant shift in the energy, because the potential enters non-linearly in the denominator of the Hamiltonian. This deficiency can, however, be approximately remedied by suitable means [33,35].

The latest major achievement in the field of elimination techniques for the small component is due to Dyall and has been worked out to an efficient computational tool for quantum chemistry within the last few years [36–39]. This method is commonly dubbed normalised elimination of the small component (NESC) and is based on the modified Dirac equation [40,41], where the small component  $\phi^S$  of the 4-spinor  $\phi$  is replaced by a pseudolarge component  $\psi^L$  defined by the relation

$$c \boldsymbol{\sigma} \cdot \mathbf{p} \psi^L = 2mc^2 \phi^S. \quad (32)$$

An insertion of this relation into the split-form of the Dirac equation, Eq. (5) and (6), yields the modified Dirac equation

$$(V - E) \phi^L + T \psi^L = 0, \quad (33)$$

$$T \phi^L + \left[ \frac{1}{4m^2 c^2} (\boldsymbol{\sigma} \cdot \mathbf{p})(V - E)(\boldsymbol{\sigma} \cdot \mathbf{p}) - T \right] \psi^L = 0, \quad (34)$$

where  $T$  is the non-relativistic kinetic energy operator. This is a pair of two coupled second-order equations relating the two components of the modified Dirac spinor  $\phi' = (\phi^L, \psi^L)$ . Since the operator  $(\boldsymbol{\sigma} \cdot \mathbf{p})/2mc$  was extracted from the small component in the definition of the pseudolarge component, the original large component  $\phi^L$  and this new *small* component  $\psi^L$  have the same symmetry properties and can thus be expanded in the same basis set. By exploiting this special feature of the matrix representation of the modified Dirac equation it is possible to preserve the proper normalisation of the large component during the elimination of the small component  $\psi^L$ . This normalised elimination procedure results in energy eigenvalues which deviate only in order  $c^{-4}$  from the correct

Dirac eigenvalues, whereas the standard (unnormalised) elimination techniques (UESC) are only correct up to order  $c^{-2}$ . In addition, the NESC method is free from the singularities which plague the UESC methods, and can be simplified systematically by a sequence of approximations [37–39], which reduce the computational cost significantly.

### 2.3. Transformation to two components

The second possibility to reduce the four-component Dirac spinor to two-component Pauli form is to decouple the Dirac equation, i.e., to transform the Dirac Hamiltonian to block-diagonal form by a suitably chosen unitary transformation  $U$ ,

$$H_{bd} = U H_D U^\dagger = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}, \quad (35)$$

with  $UU^\dagger = 1$ . In the following, we shall call a transformation of the Dirac Hamiltonian  $H_D$  of this kind an exact Foldy–Wouthuysen (EFW) transformation, and the corresponding transformed Dirac spinor a Foldy–Wouthuysen (FW) spinor. Similar to the Hamiltonian, also the spinor is simplified by this unitary transformation and has only one non-vanishing 2-spinor component, i.e.,

$$\tilde{\phi} = U\phi = \begin{pmatrix} \tilde{\phi}^L \\ \tilde{\phi}^S \end{pmatrix} \quad (36)$$

with  $\tilde{\phi}^S = 0$  for class I solutions and  $\tilde{\phi}^L = 0$  for class II solutions. Note that the two ‘effective’ operators  $h_+$  and  $h_-$  reproduce the entire energy spectrum of the Dirac operator  $H_D$ .

Before deriving the explicit form of the matrix  $U$  in terms of the operator  $X$  it should be mentioned that the spectrum of the Dirac operator  $H_D$  is invariant under arbitrary similarity transformations, i.e., non-singular (invertible) transformations  $U$ , whether they are unitary or not. But only unitary transformations conserve the normalisation of the Dirac spinor and leave scalar products and matrix elements invariant. Therefore a restriction to unitary transformations is inevitable as soon as one is interested in properties of the wavefunction. Furthermore, the problem experiences a great technical simplification by the choice of a unitary transformation, since the inverse transformation  $U^{-1}$  can in general hardly be accomplished if  $U$  was not unitary.

Employing the most general ansatz for the unitary matrix  $U$ ,

$$U = \begin{pmatrix} U_{11} & U_{12} \\ U_{21} & U_{22} \end{pmatrix}, \quad (37)$$

the requirement  $\tilde{\phi}^S = 0$  for electronic (class I) solutions leads to the condition

$$[U_{21} + U_{22}X]\phi^L = 0, \quad (38)$$

which has to be satisfied for all 2-spinors  $\phi^L$  under consideration. This can only be achieved by the operator identity

$$U_{21} = -U_{22}X. \quad (39)$$

Similarly, the requirement  $\tilde{\phi}^L = 0$  for positronic (class II) solutions yields together with  $X^\dagger = -Y$  the relation

$$U_{12} = U_{11}X^\dagger. \quad (40)$$

Finally, the form of  $U_{11}$  and  $U_{22}$  is determined by the unitarity condition  $UU^\dagger = 1$ , which is only satisfied if

$$U_{11} = e^{i\xi}(1 + X^\dagger X)^{-1/2}, \quad \xi \in [0, 2\pi[, \quad (41)$$

and

$$U_{22} = e^{i\varphi}(1 + XX^\dagger)^{-1/2}, \quad \varphi \in [0, 2\pi[, \quad (42)$$

where  $\xi$  and  $\varphi$  are arbitrary phase factors. Since a global phase is obviously insignificant for the construction of a unitary matrix, we may set  $\xi = 0$  without loss of generality and confine our considerations to the relative phase between  $U_{11}$  and  $U_{22}$  only. We thus have derived the most general form of the unitary matrix  $U$  that achieves a block-diagonalisation of the Dirac Hamiltonian  $H_D$ ,

$$U = U(X) = \begin{pmatrix} (1 + X^\dagger X)^{-1/2} & (1 + X^\dagger X)^{-1/2} X^\dagger \\ -e^{i\varphi}(1 + XX^\dagger)^{-1/2} X & e^{i\varphi}(1 + XX^\dagger)^{-1/2} \end{pmatrix}. \quad (43)$$

In the literature mainly two choices for the relative phase  $\varphi$  occur. In their original work [13], where the form of  $U = U(X)$  was derived for the first time, Heully and co-workers have chosen  $\varphi = \pi$ , which results in an hermitean form of  $U$ . In contrast, in most of the latest publications, e.g. in [14,33,38], the choice

$\varphi=0$  is preferred. However, neither the operators nor the spectrum are affected by the choice of  $\varphi$ , and we will therefore not fix this phase for the moment, in order to demonstrate the independence of the results of the choice of  $\varphi$ .

Once the form of the unitary matrix  $U$  is known, one can immediately calculate the EFW Hamiltonian  $H_{bd}$  given by Eq. (35). Its components are

$$h_+ = \frac{1}{\sqrt{1+X^\dagger X}} \left\{ V + c \boldsymbol{\sigma} \cdot \mathbf{p} X + X^\dagger c \boldsymbol{\sigma} \cdot \mathbf{p} + X^\dagger (V - 2mc^2) X \right\} \frac{1}{\sqrt{1+X^\dagger X}} \quad (44)$$

and

$$h_- = \frac{1}{\sqrt{1+XX^\dagger}} \left\{ V - 2mc^2 - c \boldsymbol{\sigma} \cdot \mathbf{p} X^\dagger - X^\dagger c \boldsymbol{\sigma} \cdot \mathbf{p} + XVX^\dagger \right\} \frac{1}{\sqrt{1+XX^\dagger}}, \quad (45)$$

where the off-diagonal elements of  $H_{bd}$  vanish due to Eq. (16). Thus we have shown, that the matrix  $U=U(X)$  defines a unitary transformation of the Dirac Hamiltonian to block-diagonal form if and only if  $X$  satisfies Eq. (16). Unfortunately, the operator  $X$  and hence the matrix  $U$  is not available in closed form, except for a few very special cases. It is therefore necessary to employ approximations like a perturbative expansion of  $U$  in a carefully chosen parameter.

The historically first attempt to achieve the block-diagonalisation of the Dirac Hamiltonian  $H_D$  is due to Foldy and Wouthuysen and dates back to 1950 [42]. The central idea of this time-honoured approach is to partition the Hamiltonian into even and odd terms and to classify these terms according to their order in  $1/mc^2$ . Even terms are block-diagonal and commute with  $\beta$ , whereas odd terms are off-diagonal and anticommute with  $\beta$ ,

$$[\mathcal{E}, \beta] = 0, \quad \{\mathcal{O}, \beta\} = 0. \quad (46)$$

Therefore the original Dirac Hamiltonian may be written as

$$H_D = (\beta - 1)mc^2 + V + c \boldsymbol{\alpha} \cdot \mathbf{p} = \mathcal{E}^{(-1)} + \mathcal{E}^{(0)} + \mathcal{O}^{(0)}, \quad (47)$$

where the superscript in parentheses denotes the order of the corresponding term in  $1/mc^2$ . The unitary transformation  $U$  given by Eq. (35) is decomposed into a sequence of unitary transformations  $U^{(i)}$ ,

$$H_{bd} = U H_D U^\dagger = \dots U^{(2)} U^{(1)} U^{(0)} H_D U^{(0)\dagger} U^{(1)\dagger} U^{(2)\dagger} \dots, \quad (48)$$

where each  $U^{(i)}$  is parametrised by the exponential ansatz  $U^{(i)} = \exp(iS_i)$  with a hermitean operator  $S_i$ , which is of leading order  $(1/mc^2)^{i+1}$ . This operator  $S_i$  is always chosen suitably in order to eliminate the lowest-order odd term resulting from the previous transformations. For example, for the first unitary transformation the choice  $S_0 = -i\beta O^{(0)}/2mc^2$  has to be made. Of course, this operator will introduce new odd terms of higher order, which have to be removed by subsequent unitary transformations. However, these transformations cannot be applied in closed form, except for the case of a free particle to be discussed below, and one has to restrict the approach to an expansion in  $1/mc^2$ , e.g. by taking advantage of the Baker–Campbell–Hausdorff relation. However, a careful analysis has shown, that the general FW transformation has several serious deficiencies. On the one hand, the resulting expressions are highly singular, except for the leading term and to some extent the first relativistic correction, and cannot be used in a variational calculation. On the other hand, the Foldy–Wouthuysen wavefunctions are no longer analytic functions of  $1/c$  in the neighbourhood of  $1/c=0$ , i.e., their non-relativistic limit is not well defined [43–46]. This is at variance with the large component  $\phi^L$  of the original Dirac spinor [47]. Therefore the general FW transformation in the presence of an external potential has essentially no practical value.

However, the situation is completely different in the case of a free particle, since the sequence of transformations given by Eq. (48) may be performed in closed form and conveniently summarised in a single operator  $U_0$ . The expansion in  $1/mc^2$  can thus be avoided, and this so-called free-particle Foldy–Wouthuysen (fpFW) transformation is given by

$$U_0 = \exp\left(\beta \frac{\boldsymbol{\alpha} \cdot \mathbf{p}}{2p} \arctan \frac{p}{mc}\right) = A_p (1 + \beta R_p), \quad (49)$$

with

$$A_p = \sqrt{\frac{E_p + mc^2}{2E_p}}, \quad R_p = \frac{c \boldsymbol{\alpha} \cdot \mathbf{p}}{E_p + mc^2} = \boldsymbol{\alpha} \cdot \mathbf{P}_p. \quad (50)$$

Note that  $U_0$  is exactly the  $U$ -matrix defined by the free-particle operator  $X_+^{V=0}$  of Eq. (17), where the arbitrary phase of Eq. (43) has been fixed to zero. A direct evaluation of Eq. (43) for the case of vanishing external potential yields a formulation of  $U_0$  in terms of  $(2 \times 2)$ -blocks,

$$U_0 = U(X_+^{V=0}) = A_p \begin{pmatrix} 1 & \boldsymbol{\sigma} \cdot \mathbf{P}_p \\ -\boldsymbol{\sigma} \cdot \mathbf{P}_p & 1 \end{pmatrix}, \quad (51)$$

which has proven to be very useful for practical calculations.

Its application to the free-particle Dirac Hamiltonian yields the desired block-diagonal form, which has already been comprehensively discussed by Foldy and Wouthuysen [42]. However, the application of the fpFW transformation has proven to be extremely useful also in the presence of an external potential. It can still be performed in closed form and yields the Hamiltonian

$$H_1 = U_0 H_D U_0^\dagger = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1, \quad (52)$$

where the subscripts at each term on the right hand side of this equation denote the order in the external potential of the corresponding term. They are given by

$$\mathcal{E}_0 = \beta E_p - mc^2, \quad (53)$$

$$\mathcal{E}_1 = A_p (V + R_p V R_p) A_p, \quad (54)$$

$$\mathcal{O}_1 = \beta A_p [R_p, V] A_p. \quad (55)$$

It is crucial to take into account that all operators containing any power of the momentum operator, e.g.  $A_p$  or  $R_p$ , do not commute with the external potential, since  $V$  operates as an integral operator according to Eq. (11). The more explicit formulation of this fpFW Hamiltonian in terms of two-dimensional blocks may also be given and reads

$$H_1 = \begin{pmatrix} H_1^{11} & H_1^{12} \\ H_1^{21} & H_1^{22} \end{pmatrix}, \quad (56)$$

where

$$H_1^{11} = E_p - mc^2 + A_p V A_p + A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p, \quad (57)$$

$$H_1^{12} = A_p [\boldsymbol{\sigma} \cdot \mathbf{P}_p, V] A_p = -H_1^{21} \quad (58)$$

$$H_1^{22} = -E_p - mc^2 + A_p V A_p + A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p. \quad (59)$$

Note that these expressions are still exact, and the only odd term  $\mathcal{O}_1$  is first order in  $V$ . Thus  $H_1$  would indeed be completely decoupled if the particle was moving freely. This may be summarised by saying that the fpFW transformation accounts for all 'kinematic' relativistic effects.

An investigation of the structure of the terms occurring in  $H_1$  reveals, that the fpFW transformation has indeed a regularising effect for the case of Coulombic



potentials. The norm of the operator  $A_p$  is always between 1 (small momenta) and  $1/\sqrt{2}$  (large momenta), whereas  $R_p$  lies always between 0 (small momenta) and 1 (large momenta). Therefore the non-essential singularity of the Coulomb potential in the neighbourhood of the nucleus will never be amplified to an essential singularity as it is the case in the general FW transformation. Furthermore, the influence of the small component is to some extent shifted into the Hamiltonian  $H_1$ , such that the magnitude of the transformed small component is significantly decreased. This is most easily seen by a restriction on the leading order in  $1/c$ . Then the relation between the large and small component of the untransformed Dirac spinor is given by

$$\phi^S \sim \frac{\boldsymbol{\sigma} \cdot \mathbf{p}}{2mc} \phi^L \sim \frac{1}{c} \phi^L. \quad (60)$$

After the fpFW transformation the magnitude of the small component as compared to the large component has decreased in leading order in  $1/c$ ,

$$\phi_1^S \sim \frac{-p^2 \boldsymbol{\sigma} \cdot \mathbf{p}}{16m^3 c^3} \phi_1^L \sim \frac{1}{c^3} \phi_1^L, \quad (61)$$

and the importance of the lower component has been diminished in the transformed spinor. This development is accompanied by the decrease of the leading order in  $1/c$  of the off-diagonal blocks of  $H_1$ . The fpFW transformation reduces the leading order of these blocks from  $c$  to  $1/c$ .

Since even terms are always block-diagonal, they can, for later convenience at the discussion of the Douglas–Kroll transformation, always be decomposed into their diagonal  $(2 \times 2)$ -blocks,

$$\mathcal{E}_k = \begin{pmatrix} \mathcal{E}_{k+} & 0 \\ 0 & \mathcal{E}_{k-} \end{pmatrix} = \begin{pmatrix} \mathcal{E}_{k+}^{\text{sf}} + \mathcal{E}_{k+}^{\text{sd}} & 0 \\ 0 & \mathcal{E}_{k-}^{\text{sf}} + \mathcal{E}_{k-}^{\text{sd}} \end{pmatrix}. \quad (62)$$

The upper matrices  $\mathcal{E}_{k+}$  contain both spin-free (sf) and spin-dependent (sd) terms, which may be separated by employing Dirac's relation Eq. (29), e.g.

$$\mathcal{E}_{1+} = \underbrace{A_p V A_p + A_p \mathbf{P}_p \cdot V \mathbf{P}_p A_p}_{\mathcal{E}_{1+}^{\text{sf}}} + \underbrace{i A_p \boldsymbol{\sigma} \cdot (\mathbf{P}_p \times V \mathbf{P}_p) A_p}_{\mathcal{E}_{1+}^{\text{sd}}}. \quad (63)$$

It should be recalled that all the operators resulting from the fpFW transformation are well defined only in momentum space, and are completely described by specifying their kernel. For example, the kernel of  $\mathcal{E}_{1+}^{\text{sf}}$  is given by

$$\mathcal{E}_{1+}^{\text{sf}}(i, j) = A_i V_{ij} A_j + A_i \mathbf{P}_i \cdot V_{ij} \mathbf{P}_j A_j, \quad (64)$$

where an obvious notation has been used. Finally, the action of  $\mathcal{E}_{1+}^{\text{sf}}$  on an arbitrary 2-spinor  $\varphi$  is defined by the integral expression

$$\mathcal{E}_{1+}^{\text{sf}} \varphi(i) = \int \frac{d^3j}{(2\pi\hbar)^3} \mathcal{E}_{1+}^{\text{sf}}(i, j) \varphi(j). \quad (65)$$

We will amply use both this notation and the fpFW transformation in the discussion of the DK method in the next section.

But we should not proceed without mentioning two other methods in order to arrive at workable and regular formulations. The first method is nowadays dubbed ‘Direct Perturbation Theory’ (DPT) and guarantees a valid limiting procedure for  $1/c \rightarrow 0$  [43,44,47–51]. Here, it is very important to consider the non-relativistic limit of the metric (essentially the normalisation requirement) and of the operator itself separately. This is most conveniently achieved by formulating the Dirac equation in terms of a scaled small component  $c\phi^S$ . This approach will comprehensively be discussed in the article of Kutzelnigg in the next chapter and thus not further be described here.

The second approach was suggested quite recently by Barysz and Sadlej in a series of papers [52–55], and makes extensive use of the  $X$ -operator formalism presented above. We will give a brief survey of their ideas using our notation introduced above, which differs from their original presentation. For a more detailed discussion employing an alternative nomenclature the interested reader is referred to the original sources. The unitary transformation  $U$ , which accomplishes the block-diagonalisation of the original Dirac Hamiltonian  $H_D$  is decomposed into a preliminary fpFW transformation  $U_0$  and a residual transformation  $U_1$ ,

$$H_{bd} = U_1 U_0 H_D U_0^\dagger U_1^\dagger = U_1 H_1 U_1^\dagger = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}, \quad (66)$$

where  $H_1$  is the fpFW Hamiltonian given by Eq. (56). The essential idea is now to parametrise the matrix  $U_1$  by the operator  $R$ , which constitutes the exact relationship between the upper and lower component of the fpFW spinor  $\phi_1$  for electronic (class I) solutions,  $\phi_1^S = R\phi_1^L$ . We have used a new symbol for this operator in order to distinguish it from the previously introduced  $X$ -operator relating the small and large component of the original, i.e., untransformed Dirac spinor  $\phi$  via Eq. (13). According to our previous reasoning the matrix  $U_1$  may then be written as

$$U_1 = \begin{pmatrix} (1 + R^\dagger R)^{-1/2} & (1 + R^\dagger R)^{-1/2} R^\dagger \\ -(1 + R R^\dagger)^{-1/2} R & (1 + R R^\dagger)^{-1/2} \end{pmatrix}, \quad (67)$$

where the arbitrary phase of Eq. (43) has again been fixed to zero. The requirement of vanishing off-diagonal blocks of  $H_{bd}$  leads to a condition imposed on the operator  $R$ ,

$$R = (H_1^{22})^{-1} \left\{ -H_1^{12} + R H_1^{11} + R H_1^{12} R \right\}, \quad (68)$$

which is the analogue of Eq. (16). As before, this is again a non-linear (quadratic) equation for  $R$  and has thus two solutions, one belonging to the electronic and the other to the positronic part of the spectrum. After insertion of the explicit expressions for the components of  $H_1$  given by Eqs. (57)–(59), this equation may be brought into the form

$$\begin{aligned} E_p R + R E_p = & -A_p [\boldsymbol{\sigma} \cdot \mathbf{P}_p, V] A_p + [A_p V A_p, R] \\ & + [A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p, R] - R A_p [\boldsymbol{\sigma} \cdot \mathbf{P}_p, V] A_p R, \end{aligned} \quad (69)$$

which can be solved numerically within a basis set approximation by suitable means. To this end, Eq. (69) has first to be multiplied by the operator  $P_p^{-1} \boldsymbol{\sigma} \cdot \mathbf{P}_p$  from the left in order to reduce it to computationally feasible form, where

$$P_p^{-1} = (\mathbf{P}_p^2)^{-1/2} \quad (70)$$

is a scalar operator. Subsequent introduction of the operator  $Q = P_p^{-1} \boldsymbol{\sigma} \cdot \mathbf{P}_p R$  and frequent use of the relation  $\boldsymbol{\sigma} \cdot \mathbf{P}_p \boldsymbol{\sigma} \cdot \mathbf{P}_p = P_p^2$  yields the equation

$$\begin{aligned} E_p Q + Q E_p = & -P_p A_p V A_p + P_p^{-1} A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p - Q A_p V A_p \\ & + P_p^{-1} A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p P_p^{-1} Q + A_p P_p V P_p A_p Q \\ & - Q A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p - Q A_p \boldsymbol{\sigma} \cdot \mathbf{P}_p V \boldsymbol{\sigma} \cdot \mathbf{P}_p A_p P_p^{-1} Q \\ & + Q A_p V A_p P_p Q \end{aligned} \quad (71)$$

for the operator  $Q = Q(R)$ , which at first sight seems to be unnecessarily complicated. However, the matrix representation of Eq. (71) has been solved exactly [54], i.e., to arbitrarily high accuracy by standard iterative techniques of matrix algebra, and the result appears to be the best representation of the operator  $R$  that can be achieved within a given basis. Therefore the goal of a complete and exact decoupling of the large and small component of the Dirac spinor has been achieved by this procedure. Note, that Eq. (71) is still non-linear and thus bears the possibility of positronic solutions for the operator  $Q$ . The choice towards the

electronic branch has to be implemented via the boundary conditions imposed on the numerical iterative technique. Essentially  $R$  and  $Q$  have to be ‘small’ operators with operator norms much smaller than unity.

Once the matrix representation of the  $R$ -operator is known, it can immediately be used to determine the matrix representation of the two-component Hamiltonian  $h_+$ , which is, of course, given by Eq. (44) and reads

$$h_+ = \frac{1}{\sqrt{1 + R^\dagger R}} \left\{ H_1^{11} + H_1^{12} R + R^\dagger H_1^{21} + R^\dagger H_1^{22} R \right\} \frac{1}{\sqrt{1 + R^\dagger R}}. \quad (72)$$

It is the exact two-component electronic Hamiltonian within the given basis set and can be used variationally in quantum chemical calculations, since due to its derivation no negative energy states may occur.

The numerical results obtained with this method are very encouraging for one-electron atoms, where the exact Dirac energy could be reproduced to arbitrarily high precision. For hydrogenic systems, however, the very complicated spin-dependent terms occurring in the right hand side of Eq. (71) do certainly not contribute, and the computational implementation of this method may be restricted to scalar terms. It is a very interesting and yet open question, if the outstanding accuracy of this method can be transferred to the many-electron case.

Besides the above-mentioned techniques to reduce the Dirac Hamiltonian to two-component form the Douglas–Kroll (DK) transformation is an established method to achieve this goal. Its second-order variant was employed to examine a variety of systems over the last 15 years with remarkable success. Variational stability, the lack of singularities, and the possibility of systematic improvement by including higher orders are only three of its salient features. Its investigation is the subject of the next section.

### 3. THE DOUGLAS–KROLL METHOD

The decoupling of the Dirac Hamiltonian  $H_D$  in the framework of the Douglas–Kroll transformation is achieved by a systematic expansion of the Hamiltonian in ascending powers of the external potential  $V$ , whereby odd terms are systematically removed step by step. This procedure imposes the restriction that this expansion shall always be possible on a suitably chosen domain of the 1-electron Hilbert space  $\mathcal{H}$ . It requires the construction of a sequence of unitary transformations  $U_i$ , ( $i = 1, 2, 3, \dots$ ) which eliminate the lowest-order odd term  $\mathcal{O}_i$  in the  $i$ th step in order to arrive at the block-diagonal Hamiltonian  $H_{bd}$ ,

$$\begin{aligned}
H_{bd} &= U H_D U^\dagger = \underbrace{\cdots U_4 U_3 U_2 U_1 U_0}_U H_D \underbrace{U_0^\dagger U_1^\dagger U_2^\dagger U_3^\dagger U_4^\dagger \cdots}_{U^\dagger} \\
&= \cdots U_4 U_3 U_2 U_1 H_1 U_1^\dagger U_2^\dagger U_3^\dagger U_4^\dagger \cdots = \sum_{k=0}^{\infty} \mathcal{E}_k.
\end{aligned} \tag{73}$$

The innermost first unitary transformation  $U_0$  is always chosen to be the fpFW transformation, which is non-singular and can be performed in closed form. Its application results in the Hamiltonian  $H_1$  given by Eq. (52), which is thus the starting point of all Douglas–Kroll approximations. It is very important, that this expansion of the Dirac Hamiltonian in powers of  $V$  is not to be confused with the highly singular expansion in  $1/c$  occurring in the FW transformation. As mentioned earlier, a series expansion in the natural relativistic parameter  $1/c$  is not justified at all, since the non-relativistic limit  $1/c \rightarrow 0$  would not be well defined within such an approach. In contrast to these problems of the FW transformation, the DK method with its inherent expansion in powers of  $V$  does always yield regular and well defined expressions. Furthermore, this series expansion is rapidly converging due to the strong suppression of higher-order terms by large energy denominators, as will be shown for DKH4, i.e., the fourth-order Douglas–Kroll approximation. Note that the notation applied to abbreviate each term is still the same as in the presentation of the FW transformation in section 2.

The original idea of this procedure dates back to 1974 and is due to Douglas and Kroll [56]. In the following years it was brought to the attention of the community and developed to a powerful computational tool for relativistic quantum chemistry [57,58].

It should be mentioned that there are only a few restrictions on the choice of the matrices  $U_i$ . Firstly they have to be unitary and analytical (holomorphic) functions on a suitable domain of  $\mathcal{H}$ , and secondly they have to permit a decomposition of  $H_{bd}$  in even terms of definite order in the external potential according to Eq. (73). It is thus possible to parametrise them without loss of generality by a power series expansion in an odd and antihermitean operator  $W_i$  of  $i$ th order in the external potential. In the following, the physical consequences of this freedom in the choice of the unitary transformations will be investigated. Therefore we shall start with a discussion of all possible parametrisations in terms of such power series expansions. Afterwards the most general parametrisation of  $U_i$  is applied to the Dirac Hamiltonian in order to derive the fourth-order

DK approximation and it will be shown that the result is independent of the chosen parametrisation. This approach has not been investigated in the literature so far. We will denote the resulting operator equations as the *generalised* Douglas–Kroll transformation. We conclude this section by a presentation of some technical aspects of the implementation of the DK Hamiltonian into existing quantum chemical computer codes.

### 3.1. General parametrisation of a unitary matrix

The most general ansatz to construct a unitary transformation  $U = f(W)$  as an analytical function of an antihermitean operator  $W$  is a power series expansion,

$$U = a_0 \mathbf{1} + a_1 W + a_2 W^2 + a_3 W^3 + \dots = a_0 \mathbf{1} + \sum_{k=1}^{\infty} a_k W^k, \quad (74)$$

which we assume to be convergent within a suitable domain. Without loss of generality we impose the restriction that the  $a_k$  may be real coefficients. Exploiting the antihermiticity of  $W$ , ( $W^\dagger = -W$ ) the power series expansion of the hermitean conjugate transformation can be given as

$$U^\dagger = a_0 \mathbf{1} - a_1 W + a_2 W^2 - a_3 W^3 + \dots = a_0 \mathbf{1} + \sum_{k=1}^{\infty} (-1)^k a_k W^k. \quad (75)$$

The coefficients  $a_k$  have to satisfy a set of constraints such that  $U$  is unitary, i.e.,  $U U^\dagger = \mathbf{1}$ .

$$\begin{aligned} U U^\dagger &= a_0^2 \mathbf{1} + a_0 \sum_{k=1}^{\infty} [1 + (-1)^k] a_k W^k + \sum_{k,l=1}^{\infty} (-1)^k a_k a_l W^{k+l} \\ &= a_0^2 \mathbf{1} + 2a_0 \sum_{k=1}^{\infty} a_{2k} W^{2k} + \sum_{k,l=1}^{\infty} a_{2k} a_{2l} W^{2(k+l)} \\ &\quad - \sum_{k,l=0}^{\infty} a_{2k+1} a_{2l+1} W^{2(k+l+1)} \\ &= a_0^2 \mathbf{1} + (2a_0 a_2 - a_1^2) W^2 + (2a_0 a_4 + a_2^2 - 2a_1 a_3) W^4 \\ &\quad + (2a_0 a_6 + 2a_2 a_4 - 2a_1 a_5 - a_3^2) W^6 \\ &\quad + (2a_0 a_8 + 2a_2 a_6 + a_4^2 - 2a_1 a_7 - 2a_3 a_5) W^8 \end{aligned}$$

$$\begin{aligned}
& + (2a_0a_{10} + 2a_2a_8 + 2a_4a_6 - 2a_1a_9 - 2a_3a_7 - a_5^2)W^{10} + \mathcal{O}(W^{12}) \\
& \stackrel{!}{=} 1.
\end{aligned} \tag{76}$$

Note that odd powers of  $W$  do not occur in this expansion because of the antihermiticity of  $W$ . With the requirement that different powers of  $W$  be linearly independent, we arrive at the following *unitarity conditions* for the coefficients:

$$a_0 = \pm 1, \tag{77}$$

$$a_2 = \frac{1}{2} a_0 a_1^2, \tag{78}$$

$$a_4 = a_0 \left( a_1 a_3 - \frac{1}{8} a_1^4 \right), \tag{79}$$

$$a_6 = a_0 \left( a_1 a_5 + \frac{1}{2} a_3^2 - \frac{1}{2} a_1^3 a_3 + \frac{1}{16} a_1^6 \right), \tag{80}$$

$$a_8 = a_0 \left( a_1 a_7 + a_3 a_5 + \frac{3}{8} a_1^5 a_3 - \frac{3}{4} a_1^2 a_3^2 - \frac{1}{2} a_1^3 a_5 - \frac{5}{128} a_1^8 \right), \tag{81}$$

$$\begin{aligned}
a_{10} = a_0 \left( a_1 a_9 + a_3 a_7 + \frac{1}{2} a_5^2 - \frac{1}{2} a_1^3 a_7 - \frac{3}{2} a_1^2 a_3 a_5 \right. \\
\left. - \frac{5}{16} a_1^7 a_3 + \frac{15}{16} a_1^4 a_3^2 + \frac{3}{8} a_1^5 a_5 - \frac{1}{2} a_1 a_3^3 + \frac{7}{256} a_1^{10} \right).
\end{aligned} \tag{82}$$

The first coefficient  $a_0$  is fixed apart from a global minus sign and can thus always be chosen as  $a_0 = 1$ . As it will be shown later, the even terms in the decoupled DK Hamiltonian do not depend on this choice for  $a_0$ . Note that all constraints imposed on lower coefficients  $a_i$ , ( $i = 0, 2, \dots, 2k$ ) have already been applied to express the condition for the next even coefficient  $a_{2k+2}$  in Eqs. (77)–(82). All odd coefficients may be chosen arbitrarily, and all even coefficients are functions of the lower odd ones, i.e.,

$$a_{2k} = f(a_0, a_1, a_3, a_5, \dots, a_{2k-1}), \quad \forall k \in \mathbf{N}. \tag{83}$$

By using the general power series expansion for  $U$  all the infinitely many parametrisations of a unitary transformation are treated on equal footing. However, the question about the equivalence of these parametrisations for application in the Douglas–Kroll method, which represents a crucial point, is more subtle and will be analysed in the next section. It is especially not clear a priori, if the antihermitean matrix  $W$  can always be chosen in the appropriate way; the mandatory properties of  $W$ , i.e., its oddness, antihermiticity and behaviour as a correct power in the external potential, have to be checked for every single transformation  $U_i$  of Eq. (73).

The radius of convergence  $R_c$  of the power series depends strongly on the choice of the odd coefficients as may be demonstrated by the following three examples, which can be given in closed form:

$$\begin{aligned} \text{a) } U &= \sqrt{1+W^2} + W : \quad R_c = 1 \\ \implies a_0 &= 1, \quad a_1 = 1, \quad a_2 = \frac{1}{2}, \quad a_4 = -\frac{1}{8}, \quad a_6 = \frac{1}{16}, \quad a_8 = -\frac{5}{128}, \quad a_{10} = \frac{7}{256}, \\ a_3 &= a_5 = a_7 = \dots = a_{2k+1} = 0 \end{aligned}$$

$$\begin{aligned} \text{b) } U &= \exp(W) : \quad R_c = \infty \\ \implies a_0 &= 1, \quad a_1 = 1, \quad a_2 = \frac{1}{2}, \quad a_3 = \frac{1}{6}, \quad a_4 = \frac{1}{24}, \quad a_5 = \frac{1}{120}, \quad a_6 = \frac{1}{720}, \\ a_7 &= \frac{1}{5040}, \quad a_8 = \frac{1}{40320}, \quad \dots \end{aligned}$$

$$\begin{aligned} \text{c) } U &= \frac{2+W}{2-W} : \quad R_c = 2 \\ \implies a_0 &= 1, \quad a_1 = 1, \quad a_2 = \frac{1}{2}, \quad a_3 = \frac{1}{4}, \quad a_4 = \frac{1}{8}, \quad a_5 = \frac{1}{16}, \quad a_6 = \frac{1}{32}, \\ a_7 &= \frac{1}{64}, \quad \dots, \quad a_k = \frac{1}{2^{k-1}}, \quad \dots \end{aligned}$$

### 3.2. The generalised Douglas–Kroll transformation

Using the general parametrisation of  $U_i$  given by Eq. (74) with the coefficients  $a_k^{(i)}$  satisfying the unitarity conditions Eqs. (77)–(82), the sequence of unitary transformations defined in equation (73) is set up and the block-diagonal Hamiltonian  $H_{bd}$  is constructed step by step. The superscript in parentheses of the coefficients  $a_k^{(i)}$  occurring in the power series expansion characterises the corresponding unitary matrix. For later convenience the odd and antihermitean expansion parameter is denoted by  $W'$  instead of  $W$ . The transformation of the fpFW Hamiltonian  $H_1$  with  $U_1$  yields

$$\begin{aligned} H_2 &= U_1 H_1 U_1^\dagger \\ &= \left[ a_0^{(1)} \mathbf{1} + \sum_{k=1}^{\infty} a_k^{(1)} W_1'^k \right] (\mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1) \left[ a_0^{(1)} \mathbf{1} + \sum_{k=1}^{\infty} (-1)^k a_k^{(1)} W_1'^k \right] \\ &= \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1^{(2)} + \mathcal{E}_2 + \mathcal{O}_2^{(2)} + \mathcal{E}_3 + \mathcal{O}_3^{(2)} + \sum_{k=4}^{\infty} \left( \mathcal{E}_k^{(2)} + \mathcal{O}_k^{(2)} \right), \quad (84) \end{aligned}$$



with

$$\mathcal{O}_1^{(2)} = \mathcal{O}_1 + a_0^{(1)} a_1^{(1)} [W'_1, \mathcal{E}_0], \quad (85)$$

$$\mathcal{E}_2 = a_0^{(1)} a_1^{(1)} [W'_1, \mathcal{O}_1] + \frac{1}{2} [a_1^{(1)}]^2 [W'_1, [W'_1, \mathcal{E}_0]], \quad (86)$$

$$\mathcal{O}_2^{(2)} = a_0^{(1)} a_1^{(1)} [W'_1, \mathcal{E}_1], \quad (87)$$

$$\mathcal{E}_3 = \frac{1}{2} [a_1^{(1)}]^2 [W'_1, [W'_1, \mathcal{E}_1]], \quad (88)$$

$$\begin{aligned} \mathcal{E}_4^{(2)} = & a_1^{(1)} a_3^{(1)} [W_1'^3, [W'_1, \mathcal{E}_0]] - \frac{1}{8} [a_1^{(1)}]^4 [W_1'^2, [W_1'^2, \mathcal{E}_0]] \\ & + a_0^{(1)} a_3^{(1)} [W_1'^3, \mathcal{O}_1] - \frac{1}{2} a_0^{(1)} [a_1^{(1)}]^3 W'_1 [W'_1, \mathcal{O}_1] W'_1. \end{aligned} \quad (89)$$

Since this presentation focuses on the fourth-order DK Hamiltonian, only those terms are explicitly given at this first stage, which are required to derive the final fourth-order even terms, and all higher-order terms are suppressed. Note that  $\mathcal{E}_0$ ,  $\mathcal{E}_1$ , and  $\mathcal{O}_1$  are independent of  $W'_1$  and thus completely determined from the very beginning. The subscript attached to each term of the Hamiltonian denotes its order in the external potential, whereas the superscript in parentheses indicates that the respective term belongs to the intermediate, partially transformed Hamiltonian with the corresponding index. Only those even terms, which will not be affected by the succeeding transformations bear no superscript and may already be identified with the corresponding terms in the expansion of  $H_{bd}$  given by Eq. (73). It is a consequence of the so-called  $(2n+1)$ -rule, that  $\mathcal{E}_2$  and  $\mathcal{E}_3$  are already completely determined after the first unitary DK transformation  $U_1$ . Therefore,  $H_{bd}$  is already defined up to  $\mathcal{E}_3$  although the second order term  $\mathcal{O}_2^{(2)}$  is still present and will be eliminated in the next transformation step.

In general, the first  $2n+1$  even terms of  $H_{bd}$  depend only on the  $n$  lowest matrices  $W'_1, W'_2, \dots, W'_n$ , i.e., they are independent in particular of all succeeding unitary transformations. This remarkable property of the even terms originates from the central idea of the DK method to choose the latest odd operator  $W'_i$  always in such a way, that the lowest of the remaining odd terms is eliminated. Therefore  $W'_1$  is chosen in order to guarantee  $\mathcal{O}_1^{(2)} = 0$ , and thus the following condition for  $W'_1$  is obtained,

$$[W'_1, \mathcal{E}_0] = -\frac{a_0^{(1)}}{a_1^{(1)}} \mathcal{O}_1, \quad (90)$$

which is satisfied if and only if the kernel of  $W'_1$  is given by

$$W'_1(i, j) = \frac{a_0^{(1)}}{a_1^{(1)}} \beta \frac{\mathcal{O}_1(i, j)}{E_i + E_j}. \quad (91)$$

This choice of  $W'_1$  satisfies all constraints, namely that it is an odd and anti-hermitean operator of first order in  $V$ . Note that  $W'_1$  depends on the beforehand arbitrarily chosen coefficients  $a_0^{(1)}$  and  $a_1^{(1)}$ , i.e., it is linear in  $a_0^{(1)}/a_1^{(1)}$ . For later convenience we therefore introduce the modified operator  $W_1$  defined by

$$W_1(i, j) = a_0^{(1)} a_1^{(1)} W'_1(i, j) = \beta \frac{\mathcal{O}_1(i, j)}{E_i + E_j}, \quad (92)$$

which is manifestly independent of the coefficients  $a_k^{(1)}$ . With this choice of  $W_1$  and by utilising relation (90) the above results may be simplified to a large extent,

$$\mathcal{E}_2 = \frac{1}{2} [W_1, \mathcal{O}_1], \quad (93)$$

$$\mathcal{O}_2^{(2)} = [W_1, \mathcal{E}_1], \quad (94)$$

$$\mathcal{E}_3 = \frac{1}{2} [W_1, [W_1, \mathcal{E}_1]], \quad (95)$$

$$\mathcal{E}_4^{(2)} = \frac{1}{8} [W_1, [W_1, [W_1, \mathcal{O}_1]]]. \quad (96)$$

It is important to note that all these terms are independent of the coefficients  $a_k$ , i.e., they are invariant under an arbitrary change of the parametrisation of  $U_1$ . The next unitary transformation  $U_2$  is applied in order to eliminate the odd term of second order,

$$\begin{aligned} H_3 &= U_2 H_2 U_2^\dagger = \left[ a_0^{(2)} \mathbf{1} + \sum_{k=1}^{\infty} a_k^{(2)} W_2'^k \right] H_2 \left[ a_0^{(2)} \mathbf{1} + \sum_{k=1}^{\infty} (-1)^k a_k^{(2)} W_2'^k \right] \\ &= \sum_{k=0}^5 \mathcal{E}_k + \sum_{k=6}^{\infty} \mathcal{E}_k^{(3)} + \sum_{k=2}^{\infty} \mathcal{O}_k^{(3)} \end{aligned} \quad (97)$$

with

$$\mathcal{O}_2^{(3)} = \mathcal{O}_2^{(2)} + a_0^{(2)} a_1^{(2)} [W'_2, \mathcal{E}_0], \quad (98)$$

$$\mathcal{E}_4 = \mathcal{E}_4^{(2)} + a_0^{(2)} a_1^{(2)} [W'_2, \mathcal{O}_2^{(2)}] + \frac{1}{2} [a_1^{(2)}]^2 [W'_2, [W'_2, \mathcal{E}_0]]. \quad (99)$$

Again,  $W_2$  is conveniently chosen to eliminate the second-order odd term  $\mathcal{O}_2^{(3)}$ , i.e., it has to satisfy the condition

$$[W'_2, \mathcal{E}_0] = -\frac{a_0^{(2)}}{a_1^{(2)}} \mathcal{O}_2^{(2)} = -\frac{a_0^{(2)}}{a_1^{(2)}} [W_1, \mathcal{E}_1], \quad (100)$$

which is guaranteed if the kernel of  $W'_2$  is given by

$$W'_2(i, j, k) = \frac{a_0^{(2)}}{a_1^{(2)}} \beta \frac{W_1(i, j) \mathcal{E}_1(j, k) - \mathcal{E}_1(i, j) W_1(j, k)}{E_i + E_k}. \quad (101)$$

Since even and odd operators obey the same multiplication rules as natural numbers, i.e., even times odd is odd, etc., this is obviously an odd and antihermitean operator of second order in the external potential, which is linear in  $a_0^{(2)}/a_1^{(2)}$ .  $W'_2$  is thus a second-order integral operator in momentum space, whose action on a spinor  $\phi$  is defined by

$$W'_2 \phi(\mathbf{p}_i) = \int \frac{d^3 \mathbf{p}_j d^3 \mathbf{p}_k}{(2\pi\hbar)^6} W'_2(\mathbf{p}_i, \mathbf{p}_j, \mathbf{p}_k) \phi(\mathbf{p}_k) = f(\mathbf{p}_i). \quad (102)$$

After introduction of the modified operator  $W_2 = a_0^{(2)} a_1^{(2)} W'_2$ , which is again independent of the chosen parametrisations of the unitary transformations, the final result for the fourth-order even term is obtained,

$$\mathcal{E}_4 = \frac{1}{8} [W_1, [W_1, [W_1, \mathcal{O}_1]]] + \frac{1}{2} [W_2, [W_1, \mathcal{E}_1]], \quad (103)$$

where we have taken advantage of Eq. (100) in order to simplify the second term. The term  $\mathcal{E}_4$  is independent of the chosen parametrisations of the two unitary transformations.

We will conclude this section with some final comments on the generalised DK approximation. First, we have shown, that the traditional choice for the parametrisation of the unitary matrices,  $U_i = \sqrt{1 + W_i^2} + W_i$ , is only one very special case of infinitely many equivalent possibilities. All these parametrisations lead to the same fourth-order DK Hamiltonian  $H_{\text{DKH4}}$ , which results

from a truncation of Eq. (73) after the term  $\mathcal{E}_4$ . Note that  $H_{\text{DKH4}}$  is still a four-component, albeit block-diagonal momentum space operator, that is completely defined by specifying its kernel. The electronic and positronic degrees of freedom are decoupled within this fourth-order approximation, and we therefore achieved the desired goal of reducing the formalism to two-component form. The electronic, i.e., upper-left  $(2 \times 2)$ -blocks of the kernels of the lowest order terms are explicitly given as

$$\mathcal{E}_{0+}(i) = E_i - mc^2, \quad (104)$$

$$\mathcal{E}_{1+}(i, j) = \underbrace{A_i(V_{ij} + \mathbf{P}_i V_{ij} \mathbf{P}_j) A_j}_{\mathcal{E}_{1+}^{\text{sf}}(i, j)} + \underbrace{i A_i \boldsymbol{\sigma} \cdot (\mathbf{P}_i \times V_{ij} \mathbf{P}_j) A_j}_{\mathcal{E}_{1+}^{\text{sd}}(i, j)}, \quad (105)$$

$$\begin{aligned} \mathcal{E}_{2+}(i, j, k) = \frac{1}{2} \{ & -A_i \boldsymbol{\sigma} \cdot \mathbf{P}_i \tilde{V}_{ij} \boldsymbol{\sigma} \cdot \mathbf{P}_j A_j A_j V_{jk} A_k \\ & + A_i \boldsymbol{\sigma} \cdot \mathbf{P}_i \tilde{V}_{ij} A_j A_j V_{jk} \boldsymbol{\sigma} \cdot \mathbf{P}_k A_k \\ & + A_i \tilde{V}_{ij} A_j P_j^2 A_j V_{jk} A_k \\ & - A_i \tilde{V}_{ij} A_j A_j \boldsymbol{\sigma} \cdot \mathbf{P}_j V_{jk} \boldsymbol{\sigma} \cdot \mathbf{P}_k A_k \\ & - A_i \boldsymbol{\sigma} \cdot \mathbf{P}_i V_{ij} \boldsymbol{\sigma} \cdot \mathbf{P}_j A_j A_j \tilde{V}_{jk} A_k \\ & + A_i \boldsymbol{\sigma} \cdot \mathbf{P}_i V_{ij} A_j A_j \tilde{V}_{jk} \boldsymbol{\sigma} \cdot \mathbf{P}_k A_k \\ & + A_i V_{ij} A_j P_j^2 A_j \tilde{V}_{jk} A_k \\ & - A_i V_{ij} A_j A_j \boldsymbol{\sigma} \cdot \mathbf{P}_j \tilde{V}_{jk} \boldsymbol{\sigma} \cdot \mathbf{P}_k A_k \}, \end{aligned} \quad (106)$$

$$\mathcal{E}_{3+}(i, j, k, l) = \frac{1}{2} \{ A_i \boldsymbol{\sigma} \cdot \mathbf{P}_i \tilde{V}_{ij} \boldsymbol{\sigma} \cdot \mathbf{P}_j A_j A_j \tilde{V}_{jk} A_k \mathcal{E}_1(k, l) + \dots, \quad (107)$$

where the abbreviation

$$\tilde{V}_{ij} = \frac{V_{ij}}{E_i + E_j} = \frac{V(\mathbf{p}_i, \mathbf{p}_j)}{\sqrt{\mathbf{p}_i^2 c^2 + m^2 c^4} + \sqrt{\mathbf{p}_j^2 c^2 + m^2 c^4}} \quad (108)$$

has been introduced, and the identity  $\boldsymbol{\sigma} \cdot \mathbf{P}_j \boldsymbol{\sigma} \cdot \mathbf{P}_j = P_j^2$  for Pauli spin matrices has been used. The expressions for higher-order kernels are hardly more complicated, but very lengthy, and will not be given here in full detail. They can easily be constructed by evaluating the expressions of the operators  $\mathcal{E}_3$  and  $\mathcal{E}_4$  given by Eqs. (95) and (103) with the help of Eqs. (54), (55), (92), and (101).

These expressions illustrate clearly, why the DK method features excellent convergence behaviour. The  $n$ th-order kernel contains  $n - 1$  factors of  $\tilde{V}$ , i.e., it is damped by a factor smaller than  $(2mc^2)^{-n+1}$ . An extension of this generalised Douglas–Kroll transformation to fifth and higher order in the external potential is subject to further investigations.

### 3.3. Aspects of the implementation

We conclude this section with some remarks on the implementation of the DK transformation into quantum chemical program packages. It is certainly one of the greatest advantages of the DK transformation that its spin-free variant can be implemented into every non-relativistic basis-set program with comparatively little effort. Only the calculation of the integrals at the very beginning has to be modified, but the subsequent SCF or correlation calculations remain unchanged, and even the most sophisticated correlation methods are available within the DK approach. Furthermore, it was shown that the modification of the one-electron integrals yields the major contribution to physical observables, as the transformation of the two-electron integrals does, in general, not lead to significant changes on relative properties [59,60]. We will therefore restrict our presentation of the implementation of the DK method to the modification of the one-electron integrals only.

The natural formulation of the DK transformation, as it was presented in the last subsection, is given in momentum space, which emerges out of the standard configuration space formulation by a Fourier transformation. The basic feature of a momentum space formulation is the diagonal form of every function of the momentum  $\mathbf{p}$ , i.e., after introduction of a basis it has a diagonal matrix representation. However, the general DK Hamiltonian  $H_{\text{DKH}_n}$  contains only terms which are functions of the quadratic momentum operator  $p^2$  instead of the linear momentum  $\mathbf{p}$ , as can be verified by inspection of the explicit expressions given by Eqs. (104)–(107). It is therefore sufficient for the evaluation of the DK Hamiltonian to replace the computationally very demanding exact Fourier transformation into momentum space by a much simpler representation where  $p^2$  is diagonal. This unitary transformation  $\Omega$  can easily be accomplished within every quantum chemical basis set program, where the matrix representation of the non-relativistic kinetic energy  $T = p^2/2m$  is already available. The desired matrix representation of  $\Omega$  can then be obtained by a diagonalisation of  $T$ , i.e.,

$$T' = \Omega T \Omega^\dagger = (t_i)_{i=1,\dots,n}, \quad (109)$$

where  $T'$  is a diagonal matrix with the eigenvalues  $t_i = p_i^2/2m$  as entries, and

where the finite basis employed in the actual calculation was assumed to consist of  $n$  Slater or Gaussian orbitals and will be denoted by

$$\chi = \{ \chi_i : \mathbf{R}^3 \rightarrow \mathbb{C}, i = 1, \dots, n \}. \quad (110)$$

The next step in the evaluation of the DK Hamiltonian is to insert the resolution of the identity

$$1 = \boldsymbol{\sigma} \cdot \mathbf{P}_j \frac{1}{P_j^2} \boldsymbol{\sigma} \cdot \mathbf{P}_j \quad (111)$$

wherever terms of the structure  $\boldsymbol{\sigma} \cdot \mathbf{P} V \dots V \boldsymbol{\sigma} \cdot \mathbf{P}$  occur, in order to reduce all terms to only a few simple expressions. Note that this procedure is exact within the given basis set representation. After subsequent restriction to scalar, i.e., spin-free terms the kernels of  $\mathcal{E}_k$  contain only computationally feasible terms, e.g.

$$\begin{aligned} \mathcal{E}_{2+}(i, j, k) = \frac{1}{2} \Big\{ & - A_i \mathbf{P}_i \tilde{V}_{ij} \mathbf{P}_j A_j A_j V_{jk} A_k \\ & + A_i \mathbf{P}_i \tilde{V}_{ij} \mathbf{P}_j A_j \frac{1}{P_j^2} A_j \mathbf{P}_j V_{jk} \mathbf{P}_k A_k \\ & + A_i \tilde{V}_{ij} A_j P_j^2 A_j V_{jk} A_k \\ & - A_i \tilde{V}_{ij} A_j A_j \mathbf{P}_j V_{jk} \mathbf{P}_k A_k \\ & - A_i \mathbf{P}_i V_{ij} \mathbf{P}_j A_j A_j \tilde{V}_{jk} A_k \\ & + A_i \mathbf{P}_i V_{ij} \mathbf{P}_j A_j \frac{1}{P_j^2} A_j \mathbf{P}_j \tilde{V}_{jk} \mathbf{P}_k A_k \\ & + A_i V_{ij} A_j P_j^2 A_j \tilde{V}_{jk} A_k \\ & - A_i V_{ij} A_j A_j \mathbf{P}_j \tilde{V}_{jk} \mathbf{P}_k A_k \Big\}. \end{aligned} \quad (112)$$

The restriction to scalar terms and hence to a one-component Hamiltonian is sometimes referred to as a ‘spin averaged’ formulation. However, the names ‘spin-free’ or ‘scalar relativistic’ formulation seem to be more appropriate. The matrix representations of all terms occurring after these manipulations are already available within every quantum chemical program package except for the  $\mathbf{P} V \mathbf{P}$  expressions. Their evaluation can, however, be reduced to the representation of the external potential via the relation

$$\langle \chi_i | \mathbf{p} \cdot V \mathbf{p} | \chi_j \rangle = \hbar^2 \langle \nabla \chi_i | V | \nabla \chi_j \rangle. \quad (113)$$

Now the DK Hamiltonian may be calculated to the desired level of accuracy. Within our finite basis set approximation the multiple integral expressions occurring at the evaluation of the momentum space operators  $\mathcal{E}_k$  are reduced to simple matrix multiplications, which are computationally not very demanding. As soon as  $H_{\text{DKH}_n}$  has been evaluated within the chosen  $p^2$ -representation, it can be transformed back to the usual configuration space representation by applying the inverse transformation  $\Omega^{-1}$ . This Hamiltonian is then available for every variational procedure without any further modifications.

#### 4. NUMERICAL RESULTS WITH DKH3 & DKH4

Currently, the scalar relativistic third- and fourth-order Hamiltonians  $H_{\text{DKH}_3}$  and  $H_{\text{DKH}_4}$  of the generalised DK method have been implemented into an atomic Hartree–Fock program based on the work by Roothaan and Bagus [61]. In the following, we present numerical results for both hydrogenic, i.e., one-electron systems for the whole periodic table and all-electron noble gas atoms up to element 118 (Eka-Rn). We have employed the relativistic universal Gaussian basis set provided by Malli et al. [62], which was augmented with additional large exponents in order to achieve sufficiently high accuracy to resolve the DKH4 correction. We have used  $c = 137.0359895$  as value for the speed of light for all our calculations.

In the first series of calculations the ground state, i.e.,  $1s$  eigenvalues of hydrogenlike systems for nuclear charges up to  $Z = 118$  were determined for the non-relativistic (n.r.) case as well as for the second- (DKH2), third- (DKH3), and fourth-order (DKH4) Douglas–Kroll approximation. We have used the point-nucleus model in order to compare our results to the analytically known exact eigenvalues resulting from the Dirac equation (DEQ). The smallest exponent of the universal Gaussian basis set is given by 0.021494, and the ratio between two subsequent exponents is approximately 2.054433. However, in order to achieve highly accurate results even for systems with very large nuclear charge  $Z$  we augmented this basis with 18 additional large exponents according to the ratio given above. The resulting basis set contained 50  $s$ -functions and exponents up to  $10^{14}$ . The numerical results for five typical systems with increasing nuclear charge are shown in Table 1.

The non-relativistic result was recovered for all calculations to very high accuracy. The very small deviation of at most  $10^{-4}\%$  has proven that the chosen basis set is able to describe the wave function close to the nucleus very well. For all values of the nuclear charge  $Z$  DKH2 represents a significant improvement over the non-relativistic value. However, for increasing values of  $Z$  DKH2 is

Table 1

1s energies for one-electron hydrogenlike systems with varying nuclear charge  $Z$  in Hartree atomic units. All calculations were performed with a relativistic universal Gaussian basis set [62] with originally 32  $s$ -functions, augmented up to 50  $s$ -functions for systems with high nuclear charge. The speed of light  $c = 137.0359895$  was used for all calculations.

$Z$	10	40	70	100	118
n.r.	-49.999943	-799.999988	-2449.999944	-4999.99977	-6961.99953
DKH2	-50.066667	-817.615749	-2630.658155	-5906.19157	-9128.64893
DKH3	-50.066743	-817.820017	-2635.262865	-5942.36914	-9234.04049
DKH4	-50.066741	-817.804855	-2634.670524	-5936.47367	-9220.03101
DEQ	-50.066742	-817.807498	-2634.846565	-5939.19538	-9230.62732

no longer able to describe the relativistic effects on the *total* energy appropriately, as for  $Z = 118$  the absolute error is about 100 hartree. For those highly relativistic systems higher-order approximations are important, and indeed, the results obtained with DKH3 and DKH4 are in much better agreement with the exact eigenvalues resulting from the Dirac equation. Therefore, one necessarily has to go beyond the established second order DK method if one is interested in highly accurate total energies of systems including heavy nuclei.

There is one further subtlety with the DKH3 results that should be mentioned explicitly. The third-order energies are always below the exact Dirac value, as can easily be seen from Table 1. This indicates that  $H_{\text{DKH3}}$  is only a variationally stable but not variational approximation to the exact electronic Hamiltonian. An extension of the DK method to fourth-order in the external potential cures this deficiency of DKH3, and we find always energies above the corresponding Dirac values. This very important feature of DKH3 has not yet been observed in the only earlier study about the third-order DK method [63]. It is only revealed by use of very large basis sets, since very high exponents are necessary to model the region very close to the nucleus in such highly charged one-electron atoms.

In order to investigate the performance of the various orders of the DK method in greater detail, it is convenient to examine the dependence of the results on the nuclear charge  $Z$  in a systematic manner and compare it to the well-known dependence of the exact Dirac eigenvalues on  $Z$ . The exact Dirac energy for  $1s_{1/2}$  levels is given by

$$E = mc^2 \left( \sqrt{1 - \gamma^2} - 1 \right), \quad (114)$$



Table 2

Taylor expansion coefficients of Eq. (116) for the  $1s$  energy of hydrogenlike atoms. The results were extracted from calculations for nuclear charges from  $Z = 1$  up to  $Z = 126$  by a least-squares fitting procedure to a power series of the type given by Eq. (116).

	$a_0$	$a_2$	$a_4$	$a_6$	$a_8$
DEQ	0.50000000	0.12500000	0.06250000	0.03906250	0.02734375
DKH2	0.5000	0.1250	0.0621		
DKH2 [64]	0.500	0.125	0.056		
DKH3	0.5000	0.1250	0.0625	0.0421	
DKH4	0.5000	0.1250	0.0625	0.0387	

where

$$\gamma = Z\alpha = \frac{Ze^2}{\hbar c} \approx \frac{Z}{137.036} \text{ a.u.} \quad (115)$$

is the usual relativistic expansion parameter. An expansion of this Dirac ground state energy in powers of  $\gamma$  yields

$$\begin{aligned} E &= -\gamma^2 mc^2 \left[ a_0 + a_2 \gamma^2 + a_4 \gamma^4 + a_6 \gamma^6 + a_8 \gamma^8 + \mathcal{O}(\gamma^{10}) \right] \\ &= -\gamma^2 mc^2 \left[ \frac{1}{2} + \frac{1}{8} \gamma^2 + \frac{1}{16} \gamma^4 + \frac{5}{128} \gamma^6 + \frac{7}{256} \gamma^8 + \mathcal{O}(\gamma^{10}) \right]. \end{aligned} \quad (116)$$

Notice that the leading term recovers the non-relativistic energy

$$E_{nr} = -\frac{1}{2} \gamma^2 mc^2 = -\frac{Z^2 e^2}{2a_B}, \quad (117)$$

where

$$a_B = \frac{\hbar^2}{me^2} \approx 0.53 \text{ \AA} \quad (118)$$

is the familiar first Bohr radius.

We have determined these Taylor expansion coefficients for DKH2, DKH3, and DKH4 by fitting the one-electron results for  $Z = 1$  up to  $Z = 126$  to the power series given by Eq. (116) in a least square manner. The results are displayed in Table 2. Our result for the coefficient  $a_4$  for DKH2 is significantly

closer to the exact value resulting from the Dirac equation than it was in an earlier study by Molzberger et al. [64]. It is most likely that this difference is due to basis set deficiencies, whereas the results obtained in the recent study have proven to be very close to the basis set limit, as has been checked by an extension of the basis set size. Due to this very satisfactory value for  $a_4$  it must be emphasised that DKH2 yields a sufficiently accurate description of scalar relativistic effects for most applications in chemistry. This is confirmed by innumerable studies performed with DKH2 in the last decade.

The transition to higher-order DK approximations reveals that DKH3 and DKH4 are even capable to reproduce the coefficient  $a_4$  exactly. DKH3 gives a quite satisfactory result for  $a_6$  as long as only its magnitude is concerned. However, due to the minus sign of Eq. (116)  $a_6$  obtained with DKH3 lies below the exact Dirac value for this coefficient. Again, this confirms the non-variational character of DKH3. The superior behaviour of DKH4 over DKH3 is documented by its capability to reproduce the coefficient  $a_6$  almost exactly from above. Our result for  $a_6$  is less than 1% off from the exact value. This analysis reinforces our earlier statement that DKH4 establishes a variational scheme. Hence, if one is interested in highly accurate relativistic calculations beyond the second-order DK approximation it is strongly recommended to pass directly to DKH4 instead of DKH3.

Besides these one-electron calculations we have performed all-electron calculations for the noble gas atoms up to element 118 (Eka-Rn). All calculations were done with the same basis set of the form  $32s29p20d15f$ . The results are presented in Table 3. The importance of a relativistic treatment in order to get exact total energies is obvious for all systems under consideration. As for the one-electron systems, DKH3 yields always the lowest total energy value of all DKH calculations.

However, the most remarkable result of these calculations is the rapidly increasing deviation of the DKH4 energies from the numerical, i.e., exact Dirac-Fock-Coulomb (DFC) results. The DFC values for the first four noble gases presented are taken from the benchmark results for point nuclei by Visscher and Dyall [65]. For Eka-Radon we have calculated the DFC energy with MOLFDIR [66] using the same basis set as for the DKH calculations. Since MOLFDIR employs a Gaussian nuclear model, we have described the desired point-like nucleus by increasing the exponent for the Gaussian nuclear charge distribution to  $10^{20}$ . The validity of this procedure was tested for Radon, where exact DFC energies are known for both a point nucleus and a Gaussian nuclear model. The resulting error was not larger in size than the error due to the finite basis set size.

Table 3

Ground state energies for all-electron noble gas atoms in atomic units. All calculations were performed with a relativistic universal Gaussian basis set [62] of the form  $32s29p20d15f$ .

elem.	Ne	Kr	Xe	Rn	Eka-Rn
Z	10	36	54	86	118
n.r.	-128.54501	-2752.05440	-7232.1363	-21866.7593	-46324.158
DKH2	-128.68467	-2788.04669	-7441.4846	-23533.4784	-54350.017
DKH3	-128.68482	-2788.29309	-7443.8892	-23567.0731	-54590.210
DKH4	-128.68481	-2788.27659	-7443.6475	-23561.9208	-54550.274
DFC <sup>a</sup>	-128.69197	-2788.88484	-7447.1628	-23611.1928	-55075.883 <sup>b</sup>

<sup>a</sup>Numerical Dirac-Fock-Coulomb (DFC) energies from [65] except for Eka-Rn.

<sup>b</sup>DFC calculation performed with MOLFDIR [66] using the basis given in the head of the table.

Our results indicate clearly that many-electron systems are insufficiently described by a scalar-relativistic implementation for one-electron terms of the DK transformation only. The larger the number of electrons and the heavier the nucleus of an atom the larger is the error in total energies obtained with DKH4. These deficiencies are clearly due to the missing DK transformation of the two-electron terms and the neglect of the spin-dependent terms. It is thus highly desirable to clarify the influence of these two points beyond the known implementations [59,60].

## 5. TRANSFORMATION OF THE WAVEFUNCTION — PICTURE CHANGE

The transformation of the Dirac Hamiltonian to two-component form is accompanied by a corresponding reduction of the wavefunction. As discussed in detail in section 2, the four-component Dirac spinor  $\phi$  will have only two non-vanishing components, as soon as the complete decoupling of the electronic and positronic degrees of freedom is achieved, and can thus be used as a two-component spinor. This feature can be exploited to calculate expectation values of operators in an efficient manner. However, this procedure requires that some precautions need to be taken care of with respect to the representation of the operators, i.e., their transition from the original  $(4 \times 4)$ -matrix representation (often referred to as the Dirac picture) to a suitable two-component Pauli repre-

sentation has to be taken into account. The neglect of this mandatory transition has amply been discussed in the recent literature [67–72] and has often been referred to as the ‘picture change effect’. In the following, we illuminate this field by giving an explicit description how atomic or molecular properties have to be calculated up to a desired level of accuracy within the generalised DK method.

Let  $U$  be the exact FW transformation defined by Eq. (35) that decouples the Dirac Hamiltonian. The transformed wavefunction for class I (electronic) solutions has thus only a non-vanishing upper component and is given by

$$\tilde{\phi} = U \phi = \begin{pmatrix} \tilde{\phi}^L \\ 0 \end{pmatrix}. \quad (119)$$

According to the basic principles of quantum mechanics, every physical observable  $Y$  within the Dirac theory is described by a self-adjoint  $(4 \times 4)$ -matrix operator, which can always conveniently be written as

$$Y = \begin{pmatrix} Y_{11} & Y_{12} \\ Y_{21} & Y_{22} \end{pmatrix}. \quad (120)$$

Its expectation value within the original, i.e., untransformed Dirac picture reads

$$\bar{Y} = \langle \phi | Y | \phi \rangle, \quad (121)$$

and can therefore easily be reformulated within a two-component scheme employing the transformed spinor  $\tilde{\phi}^L$  only,

$$\begin{aligned} \bar{Y} &= \langle \phi | U^\dagger U Y U^\dagger U | \phi \rangle = \langle \tilde{\phi} | U Y U^\dagger | \tilde{\phi} \rangle \\ &= \langle \tilde{\phi}^L | [U Y U^\dagger]_{11} | \tilde{\phi}^L \rangle, \end{aligned} \quad (122)$$

where  $[U Y U^\dagger]_{11}$  denotes the upper left block of the transformed  $(4 \times 4)$ -operator. This expression is still exact and no approximation has been introduced yet. However, in two-component quantum chemical calculations of expectation values this unitary transformation of the operator  $Y$  is often not taken into account. Instead, the quantity

$$\bar{y} = \langle \tilde{\phi}^L | Y_{11} | \tilde{\phi}^L \rangle \quad (123)$$

is calculated, i.e., the change of picture for the operator  $Y$  is neglected completely. As a consequence, the difference  $\bar{Y} - \bar{y}$  has been called the ‘picture

change effect' of the transition from the four-component to the two-component representation.

From these considerations it should be unambiguously clear that the change of picture is an artificial effect resulting from basic properties of the theory of unitary linear transformations, rather than a complicated feature of the two-component theories. It has already been discussed by Newton and Wigner [73] and Foldy and Wouthuysen [42] and has even found its way into standard physics textbooks about the Dirac equation, e.g. [74].

In general, whenever a unitary transformation is applied to the Hamiltonian in order to block-diagonalise it, but not to other physical observables, some picture change effect will occur. It will thus be a very special situation if this effect is tiny and can be neglected without loss of accuracy. However, many discussions in the literature list special operators, for which it seems to be important to consider the picture change effect. The complement of these lists is more appropriate since those operators should be mentioned, for which a vanishing or at least negligible picture change effect is observed. This discussion may be compared to the treatises about relativistic effects in quantum chemistry. There the occurrence of relativistic effects is frequently emphasised as a special feature of a particular system. However, it is a more special situation if a system does not exhibit relativistic effects and can thus be described by the non-relativistic Schrödinger approximation to the exact relativistic theory.

During the last decade, a plethora of careful studies has appeared, where the magnitude of the picture change effect for various systems of chemical interest has been analysed. However, following the general philosophy of this book to focus mainly on formal theoretical developments rather than on numerical results obtained for particular systems, we will only briefly summarise the main results of these numerical investigations. For more detailed information the interested reader is referred to the original sources, e.g. [68,71,75–80].

In general, the picture change effect will be significant for operators which assume large values in the vicinity of the nuclei, e.g. electric field gradients at heavy nuclei. Since calculated electric field gradients are used to determine the nuclear quadrupole moments from molecular quadrupole coupling constants, the so-called molecular values of nuclear quadrupole moments are very sensitive to picture change effects. For other observables, e.g. dipole moment and polarisability derivatives with respect to nuclear coordinates no definite statement about the importance of the picture change effect seems possible at the moment.

We conclude this section with some remarks concerning the accuracy of ex-

pectation values of observables within the generalised DK approximation. It was shown in section 3, that the derivation of the fourth-order DK Hamiltonian  $H_{\text{DKH4}}$  requires only the first two unitary transformations  $U_1$  and  $U_2$  to be applied. This is a consequence of the  $(2n+1)$ -rule of the DK method and implies that the energy, i.e., the expectation value of the Hamiltonian, is already accurate through the fourth-order in the external potential. However, for a general observable  $Y$ , which is assumed to be independent of the potential  $V$ , no  $(2n+1)$ -rule holds, and its expectation value within the fourth-order DK approximation will be accurate only through second-order in the external potential,

$$\begin{aligned}\bar{Y} &= \langle \tilde{\phi}^L | [U_2 U_1 U_0 Y U_0^\dagger U_1^\dagger U_2^\dagger]_{11} | \tilde{\phi}^L \rangle + \mathcal{O}(V^3) \\ &= \left\langle \tilde{\phi}^L \left| \left[ Y_0 + [W_1, Y_0] + [W_2, Y_0] + \frac{1}{2} [W_1, [W_1, Y_0]] \right] \right| \tilde{\phi}^L \right\rangle, \quad (124)\end{aligned}$$

where the general parametrisation of the unitary matrices given by Eq. (74) has been used and  $Y_0 = U_0 Y U_0^\dagger$  is the fpFW transform of the operator  $Y$ .  $W_1$  and  $W_2$  are the odd operators introduced at the derivation of the DK Hamiltonian in section 3. Eq. (124) is already a fairly complicated expression for  $\bar{Y}$ , however it is only accurate up to second-order. If one liked to achieve the same accuracy for  $\bar{Y}$  as for the energy expectation value  $\langle H_{\text{DKH4}} \rangle$ , one would have to apply the first four unitary transformations  $U_i$ , ( $i = 1, \dots, 4$ ) which is truly a discouraging perspective. However, it is important to be aware of these subtleties if one is interested in the calculation of highly accurate atomic or molecular properties.

## 6. CONCLUSIONS AND PERSPECTIVES

In this account, we have presented both the basic theory of two-component methods in quantum chemistry and new developments achieved within the framework of the generalised DK transformation, which have not yet been described elsewhere. Two-component methods have several advantages when compared to the traditional four-component formulation, which is the well-established covariant description of relativistic quantum mechanics. On the one hand, the computational requirements are significantly reduced by transition to a two-component formulation. While on the other hand, the full four-component machinery is primarily necessary to describe both electronic and positronic degrees of freedom, only the electronic degrees of freedom need to be treated explicitly for chemical purposes. It appears therefore justified to claim that two-component formulations are the natural description for relativistic quantum *chemistry*.

There are two major approaches to reduce the Dirac Hamiltonian to two-component form. The various regular elimination techniques have been developed to highly sophisticated and very successful methods, which are widely used by the community. The other approach comprises the various unitary transformation methods, which amount either to expansions in  $1/c$  as for the FW transformation or to expansions in powers of the external potential  $V$  as for the DK approximations. In addition, we have presented a very general extension of the traditional DK approximation to arbitrary unitary transformations.

We have therefore explicitly derived all possible parametrisations of a unitary matrix and have subsequently employed this most general ansatz to investigate the higher-order terms of the generalised DK approximation. Up to fourth-order in the external potential  $V$ , the DK Hamiltonian  $H_{\text{DKH4}}$  was shown to be independent of the chosen parametrisation. The numerical results for both one- and many-electron atoms are very encouraging and revealed superior performance of the fourth-order method as compared to the third-order approximation. Especially the underestimation of total binding energies within the third-order approximation is cured by an extension to DKH4.

It was further shown that both the transformation of the two-electron terms occurring in the Hamiltonian and the explicit treatment of spin-dependent terms is crucial for the calculation of total energies and inner-shell properties of many-electron atomic or molecular systems. If the extraordinarily high accuracy obtained with DKH4 for one-electron systems should be preserved even for the many-electron case, it appears not to be sufficient to restrict on a scalar relativistic approximation to the transformation of the one-electron terms only. The inclusion of the transformation of the many-electron terms into the generalised DK method as well as its extension to higher order is in progress. With this machinery even molecular calculations of very high accuracy should be accessible to two-component methods, since the DK procedure can be merged with correlated methods in a straightforward way. At the moment only four-component program packages are able to achieve this goal. These developments appear to bear the possibility to open the door towards computationally feasible high-precision calculations of chemically interesting molecular systems within the framework of relativistic quantum chemistry.

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