The generalized Douglas–Kroll transformation

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We derive the most general parametrization of the unitary matrices in the Douglas–Kroll (DK) transformation sequence for relativistic electronic structure calculations. It is applied for a detailed analysis of the generalized DK transformation up to fifth order in the external potential. While DKH2–DKH4 are independent of the parametrization of the unitary matrices, DKH5 turns out to be dependent on the third expansion coefficient of the innermost unitary transformation which is carried out after the initial free-particle Foldy–Wouthuysen transformation. The freedom in the choice of this expansion coefficient vanishes consistently if the optimum unitary transformation is sought for. Since the standard protocol of the DK method is the application of unitary transformations to the one-electron Dirac operator, we analyze the DKH procedure up to fifth order for hydrogenlike atoms. We find remarkable accuracy of the higher-order DK corrections as compared to the exact Dirac ground state energy. In the case of many-electron atomic systems, we investigate the order of magnitude of the higher-order corrections in the light of the neglect of the DK transformation of the two-electron terms of the many-particle Hamiltonian. A careful analysis of the silver and gold atoms demonstrates that both the fourth- and fifth-order one-electron DK transformation yield a smaller contribution to the total electronic energy than the DK transformation of the two-electron terms. In order to improve significantly on the third-order correction DKH3, it is thus mandatory to include the DK transformation of the two-electron terms as well as the spin-dependent terms before proceeding to higher orders in the transformation of the one-electron terms. However, an analysis of the ionization energies of these atoms indicates that already DKH3 yields a highly accurate treatment of the scalar-relativistic effects on properties. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1515314]

I. INTRODUCTION

Contemporary chemistry is aware of a large number of systems, whose theoretical description requires an extension of the framework of nonrelativistic quantum mechanics. For example, the spectral properties and binding energies of heavy element compounds and transition-metal complexes are strongly governed by relativistic effects. Those intrinsically relativistic systems require the framework of relativistic quantum chemistry, which is based on the Dirac equation,

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

where V is the attractive external potential of Coulomb type, $V(\boldsymbol{r})=-Ze^2/r$, or alternatively a potential derived from an extended nuclear charge distribution. In order to get electronic binding energies comparable to the nonrelativistic Schrödinger theory the energy scale is shifted by the rest energy mc^2 of the electron. Employing the standard representation of the Dirac algebra the four Dirac matrices may be given as

$$\boldsymbol{\alpha}=\begin{pmatrix}0 & \boldsymbol{\sigma}\\ \boldsymbol{\sigma} & 0\end{pmatrix},\quad \beta=\begin{pmatrix}\mathbf{1} & 0\\ 0 & \mathbf{-1}\end{pmatrix} \tag{2}$$

with

$$\sigma_x=\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix},\quad \sigma_y=\begin{pmatrix}0 & -\mathrm{i}\\ \mathrm{i} & 0\end{pmatrix},\quad \sigma_z=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix} \tag{3}$$

being the familiar Pauli spin-matrices. Since 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 scale of the valence shell, it is a very good approximation to integrate them out at the very beginning, and thus neglect all quantum electrodynamical corrections. However, even within this so-called no-pair approximation the resulting formalism based on Eq. (1) does still consist of four coupled differential equations, including both spin-free and spin-dependent terms and mixing all four components of the Dirac 4-spinor ϕ. As a consequence, the computational cost of these four-component methods is significantly increased as compared to nonrelativistic calculations, and they are only applicable to systems of rather modest size. Currently, molecules containing more than two symmetry nonredundant heavy-element atoms are hardly accessible for these methods (compare Ref. 1 for a review of these methods). It is therefore a highly desirable goal to find another representation of the Dirac spinor, where the upper, ϕ^L, and lower, ϕ^S, components are decoupled and where the separation of computationally expensive spin-dependent terms is straightforward. The resulting scalar-relativistic two-

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component theories, which yield highly accurate results if spin–orbit coupling can be neglected, are much better behaved from a computational point of view and can even be applied to large transition-metal complexes with hundreds of electrons for comparatively little cost.

Over the last two decades two major branches of relativistic two-component quantum chemistry have emerged, which have extensively been discussed in recent reviews.[2,3] The so-called elimination techniques exploit the fact that for electronic solutions of Eq. (1) in the case of weak potentials the small component ϕ^S is suppressed by a factor of $(2mc)^{-1}$ with respect to the large component ϕ^L. Based on the general theory of effective Hamiltonians,[4,5] this facilitates the so-called regular approximations (RA),[6,7] whose zeroth- (ZORA) and first-order (FORA) variants have successfully been applied to a variety of systems.[8–11] Recently, Dyall took advantage of the modified Dirac equation[12,13] and suggested the method of normalized elimination of the small component (NESC).[14–17]

The second class of methods employs a suitably chosen unitary transformation U in order to annihilate the coupling between the upper and lower components, i.e., to remove the odd (off-diagonal) terms of the Hamiltonian. This yields a decoupled, block-diagonal transformed Hamiltonian,

$$H_{\mathrm{bd}} = U H_D U^{\dagger} = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}, \tag{4}$$

which does still act on wave functions being based on four-component spinors, but where we now have the possibility to focus on the positive-energy part of these spinors, i.e., the upper-left part h_+ of the Hamiltonian H_{bd} and work with two-component objects only. The first attempt to achieve this block-diagonalization of the Hamiltonian is due to Foldy and Wouthuysen in 1950,[18] and utilizes an expansion in $1/mc^2$ while employing the momentum representation of the Hamiltonian. However, this expansion gives rise to highly singular terms in the presence of an external potential, which may therefore not be used in a variational calculation. Furthermore, the Foldy–Wouthuysen wave functions are no longer analytic functions of $1/c$ in the neighborhood of $1/c=0$,[19–22] at variance with the large component ϕ^L of the original Dirac spinor,[23] resulting in an ill-defined nonrelativistic limit. Only the so-called free-particle Foldy–Wouthuysen (fpFW) transformation

$$U_0 = A_p(1+\beta R_p), \tag{5}$$

with

$$A_p = \sqrt{\frac{E_p + mc^2}{2E_p}}, \quad E_p = \sqrt{\boldsymbol{p}^2c^2 + m^2c^4}, \tag{6}$$

$$R_p = \frac{c\,\boldsymbol{\alpha}\cdot\boldsymbol{p}}{E_p + mc^2} = \boldsymbol{\alpha}\cdot\boldsymbol{P}_p = \mathcal{R}_p\boldsymbol{\alpha}\cdot\boldsymbol{p}, \tag{7}$$

may be used in a way avoiding expansion in $1/c$. It yields the Hamiltonian

$$H_1 = U_0 H_D U_0^{\dagger} = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1, \tag{8}$$

where each term may be uniquely classified according to its diagonal (even) or off-diagonal (odd) form and to its order in the external potential, which is denoted by the subscripts at each term on the right hand side of this equation. The explicit form of this fpFW Hamiltonian reads

$$\mathcal{E}_0 = \beta E_p - mc^2, \tag{9}$$

$$\mathcal{E}_1 = A_p(V + R_p\, V R_p)A_p, \tag{10}$$

$$\mathcal{O}_1 = \beta A_p[R_p, V]A_p. \tag{11}$$

After this initial fpFW transformation the lowest-order odd term $\mathcal{O}_1$ is first order in the external potential, instead of zeroth-order as in the original Hamiltonian H_D. These expressions for the terms of the fpFW Hamiltonian H_1 are only well-defined in momentum space, where the external potential V, and hence the first-order operators $\mathcal{E}_1$ and $\mathcal{O}_1$ act as nonlocal integral operators instead of local, multiplicative operators, e.g.,

$$\mathcal{E}_1\,\phi(\boldsymbol{p}_i) = \int \frac{\mathrm{d}^3p_j}{(2\pi\hbar)^3}\mathcal{E}_1(\boldsymbol{p}_i,\boldsymbol{p}_j)\,\phi(\boldsymbol{p}_j). \tag{12}$$

That is, the action of the integral operator $\mathcal{E}_1$ is completely determined as soon as its kernel is specified, which may immediately be given employing an obvious shorthand notation,

$$\mathcal{E}_1(i,j) = A_iV_{ij}A_j + A_iR_iV_{ij}R_jA_j. \tag{13}$$

The stepwise elimination of the respective lowest-order odd term of the Hamiltonian by suitably chosen unitary transformations is the central idea of the Douglas–Kroll (DK) transformation. The Hamiltonian is thus expanded in even terms of ascending order in the external potential V, whereby odd terms are systematically removed step by step. For this purpose the unitary transformation U of Eq. (4) is decomposed into a sequence of unitary transformations U_i, $(i=0,1,2,3,\ldots)$ which eliminate the lowest-order odd term $\mathcal{O}_i$ in the ith step in order to arrive at the block-diagonal Hamiltonian H_{bd},

$$\begin{aligned} H_{\mathrm{bd}} &= U H_D U^{\dagger} \\ &= \cdots U_4 U_3 U_2 U_1 \;\; H_1 \;\; U_1^{\dagger} U_2^{\dagger} U_3^{\dagger} U_4^{\dagger}\cdots \\ &= \sum_{k=0}^{\infty} \mathcal{E}_k \end{aligned} \tag{14}$$

$$= \sum_{k=0}^{\infty} \begin{pmatrix} \mathcal{E}_{k+} & 0 \\ 0 & \mathcal{E}_{k-} \end{pmatrix} = \sum_{k=0}^{\infty} \begin{pmatrix} \mathcal{E}_{k+}^{\mathrm{sf}} + \mathcal{E}_{k+}^{\mathrm{sd}} & 0 \\ 0 & \mathcal{E}_{k-}^{\mathrm{sf}} + \mathcal{E}_{k-}^{\mathrm{sd}} \end{pmatrix}. \tag{15}$$

The innermost first unitary transformation U_0 is always chosen to be the fpFW transformation yielding H_1, since it can be performed in closed form and achieves exactly the desired first step. The (4×4)-matrix operators $\mathcal{E}_k$ consist of two two-dimensional operators $\mathcal{E}_{k+}$ and $\mathcal{E}_{k-}$, which may always be decomposed into spin-free (sf) and spin-dependent (sd) terms, respectively. The DK method does always yield regular, i.e., nonsingular and well-defined expressions, which are variationally stable, and establish the possibility of systematic improvement by inclusion of higher orders. Furthermore, as will be demonstrated in the third section, this series ex-

pansion is rapidly converging due to the strong suppression of higher-order terms by large energy denominators. Before proceeding, we should not forget to mention that recently other transformation techniques have been proposed, which achieve the block-diagonalization of the Hamiltonian by alternative methods.[24,25] The applicability of these approaches is currently subject to extensive investigations.[26,27]

The original idea of the DK decoupling procedure of the Dirac Hamiltonian dates back to 1974 and is due to Douglas and Kroll.[28] In the following years it was brought to the attention of the community and developed to a powerful computational tool for relativistic quantum chemistry.[29,30] Its second-order variant, DKH2, was employed to examine a variety of systems over the last 15 years with remarkable success.

There are only a few restrictions on the choice of the matrices U_i. First, they have to be unitary and analytic (holomorphic) functions on a suitable domain of the one-electron Hilbert space $\mathcal{H}$, and, second, they have to permit a decomposition of H_{bd} in even terms of definite order in the external potential according to Eq. (14). It is thus possible to parametrize U_i without loss of generality by a power-series expansion in an odd and antihermitean operator W_i of ith order in the external potential, where unitarity of the resulting power series is the only constraint. Up to now, only two very special parametrizations of the transformations U_i have so far been discussed in the literature: Most frequently the *square root* parametrization $U_i=\sqrt{1+W_i^2}+W_i$ has been employed,[28–30] and recently it was pointed out that one could equally well use the *exponential* ansatz $U_i=\exp(W_i)$.[31] In the following, we investigate the physical consequences of this freedom in the choice of the unitary transformations. Therefore, we start with a discussion of all possible parametrizations of a unitary transformation in terms of such power series expansions in Sec. II. Since one always has to truncate the series expansions in the DK procedure, we will carefully study the consequences of truncating such power series expansions after a finite number of terms. In Sec. III, this principle is applied to the Dirac Hamiltonian in order to derive H_{DKH3} to H_{DKH5}, i.e., the third, fourth, and fifth-order DK Hamiltonians employing the most general unitary parametrization of U_i. The resulting operator equations will be denoted as the *generalized* Douglas–Kroll (DK) transformation, in order to distinguish them from the restricted class of transformations that have so far been discussed in the literature. In Sec. IV, numerical results for both one-electron and many-electron atomic systems are discussed, and the binding energies of hydrogenlike atoms are compared to the exact values resulting from the Dirac equation. The effect of the higher-order DK corrections on both total electronic energies and relative properties is compared to the effect of the DK transformation of the two-electron terms of the many-particle Hamiltonian. This discussion is concluded in Sec. V. The Appendix describes aspects of implementation and computational techniques.

II. GENERAL PARAMETRIZATION OF A UNITARY TRANSFORMATION

A. Exact unitary transformations

In this section the most general parametrization of the unitary transformations U_i $(i=1,2,\dots)$ employed in the DK transformation sequence defined by Eq. (14) is derived. As mentioned earlier, these unitary matrices are only beneficial for the DK procedure, if they are constructed as an analytic function $U_i=f(W_i)$ of an odd and anti-Hermitian operator W_i, which is of ith order in the external potential. In order to simplify the notation, we will drop the subscript i of both the unitary matrices U_i and the odd operators W_i in this section and simply use the abbreviations U and W. However, the matrix U of this section must not be confused with the overall unitary transformation U of Eq. (14), which is the product of all DK transformations U_i. One may always think of U as one particular transformation of the DK sequence, e.g., the innermost unitary transformation U_1 immediately following the initial fpFW transformation.

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

$$U=a_0\,\mathbf{1}+a_1W+a_2W^2+a_3W^3+\cdots=a_0\,\mathbf{1}+\sum_{k=1}^{\infty}a_kW^k, \tag{16}$$

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 Hermitian conjugate transformation is given as

$$\begin{aligned}U^\dagger&=a_0\,\mathbf{1}-a_1W+a_2W^2-a_3W^3+\cdots\\&=a_0\,\mathbf{1}+\sum_{k=1}^{\infty}(-1)^k a_kW^k.\end{aligned} \tag{17}$$

In order to construct a unitary transformation, i.e., $U\,U^\dagger=\mathbf{1}$, the coefficients a_k have to satisfy a set of constraints, which may be found by calculating

$$\begin{aligned}U\,U^\dagger=a_0^2\,\mathbf{1}&+(2a_0a_2-a_1^2)W^2+(2a_0a_4+a_2^2\\&-2a_1a_3)W^4+(2a_0a_6+2a_2a_4-2a_1a_5-a_3^2)W^6\\&+(2a_0a_8+2a_2a_6+a_4^2-2a_1a_7-2a_3a_5)W^8\\&+(2a_0a_{10}+2a_2a_8+2a_4a_6-2a_1a_9-2a_3a_7\\&-a_5^2)W^{10}+\mathcal{O}(W^{12})\overset{!}{=}\mathbf{1}.\end{aligned} \tag{18}$$

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:

$$a_0=\pm 1, \tag{19}$$

$$a_2=\tfrac{1}{2}a_0\,a_1^2, \tag{20}$$

$$a_4=a_0(a_1a_3-\tfrac{1}{8}a_1^4), \tag{21}$$

$$a_6 = a_0(a_1 a_5 + \tfrac{1}{2}a_3^2 - \tfrac{1}{2}a_1^3 a_3 + \tfrac{1}{16}a_1^6), \tag{22}$$

$$a_8 = a_0(a_1 a_7 + a_3 a_5 + \tfrac{3}{8}a_1^5 a_3 - \tfrac{3}{4}a_1^2 a_3^2 - \tfrac{1}{2}a_1^3 a_5 - \tfrac{5}{128}a_1^8), \tag{23}$$

$$a_{10} = a_0(a_1 a_9 + a_3 a_7 + \tfrac{1}{2}a_5^2 - \tfrac{1}{2}a_1^3 a_7 - \tfrac{3}{2}a_1^2 a_3 a_5 - \tfrac{5}{16}a_1^7 a_3 + \tfrac{15}{16}a_1^4 a_3^2 + \tfrac{3}{8}a_1^5 a_5 - \tfrac{1}{2}a_1 a_3^3 + \tfrac{7}{256}a_1^{10}). \tag{24}$$

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 $(i = 0,2,\ldots,2k)$ have already been applied to express the condition for the next even coefficient a_{2k+2} in Eqs. (19)–(24). Therefore all odd coefficients may be chosen arbitrarily, and all even coefficients are functions of the lower odd ones, i.e.,

$$a_{2k} = f(a_0, a_1, a_3, a_5, \ldots, a_{2k-1}), \quad \forall k \in \mathbb{N}. \tag{25}$$

By using the general power series expansion for U all the infinitely many parametrizations of a unitary transformation are treated on equal footing. However, the question about the equivalence of these parametrizations for application in the Douglas–Kroll method, which represents a crucial point, is more subtle and will be analyzed in the next section. It is furthermore not clear *a priori*, if the anti-Hermitian matrix W can always be chosen in the appropriate way; the mandatory properties of W, i.e., its oddness, antihermiticity and behavior as a certain power in the external potential, have to be checked for every single transformation U_i of Eq. (14) applied to the Dirac Hamiltonian.

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 very special three examples, which can be given in closed form:

(a) Square root parametrization: $U = \sqrt{1+W^2} + W$, $R_c = 1$,
(b) Cayley parametrization: $U = (2+W)/(2-W)$, $R_c = 2$,
(c) Exponential function parametrization: $U = \exp(W)$, $R_c = \infty$.

As long as exact unitary transformations U, i.e., infinite power series with coefficients a_k satisfying the unitarity conditions given above, are applied to transform the Hamiltonian, the energy eigenvalues of the transformed Hamiltonian $H_{\mathrm{DKHn}} = UH_D U^\dagger$ will exactly be the same as of the original Hamiltonian H_D. Therefore, the eigenvalues $E = \langle H_{\mathrm{bd}} \rangle = \langle H_{\mathrm{DKH}\infty} \rangle$ of the completely decoupled Hamiltonian H_{bd} will certainly not depend on the choice of the odd coefficients a_{2k+1}. All infinitely-many different unitary parametrizations derived above are completely equivalent in this sense. It is important to note, however, that the individual even $\mathcal{E}_k$ terms of the infinite sum given in Eq. (14) may in general depend on the chosen coefficients of the power series expansions of the unitary transformations U_i.

B. Approximately unitary transformations

However, in actual applications of the DK transformation the power series expansions of the matrices U_i always have to be truncated after a finite number of terms, resulting in an approximate unitary transformation. As a consequence, the resulting transformed Hamiltonian H_{DKHn} is only block-diagonal up to a certain order in the external potential, and its eigenvalues will both slightly differ from the exact ones and may depend on the coefficients a_k. It is thus very important to fix the odd coefficients in the best possible way, which would be to minimize the deviation of the eigenvalues of the transformed Hamiltonian H_{DKHn} (obtained with the truncated expansion for U_i) from the eigenvalues of the corresponding nth order approximation to H_{bd} given by Eq. (14). For this purpose we shall assume that this may the better be achieved the more unitary the transformations U_i are, i.e., the smaller the operator norm $|U_i U_i^\dagger - \mathbf{1}|$ is. In the following we will exploit this principle to determine the optimal parametrization of the unitary matrices U_i $(i = 1,2,\ldots)$ in order to derive the decoupled DK Hamiltonians H_{DKHn}, which are correct up to nth order in the external potential.

Since on the one hand the fpFW Hamiltonian H_1 does not contain a zeroth-order odd term and on the other hand W has to be an odd operator by construction, the derivation of the second- and third-order DK approximation requires at most a consideration of the expansion of U up to second order in W only, i.e.,

$$U = a_0 \mathbf{1} + a_1 W + a_2 W^2. \tag{26}$$

To this order the minimization of the deviation of $UU^\dagger$ from the identity, $UU^\dagger - \mathbf{1} = \frac{1}{4}a_1^4 W^4$, yields $a_1 = 0$. Due to the unitarity conditions all other coefficients would automatically vanish as well, and U would be the identity transformation. The coefficient a_1 has thus necessarily to be chosen different from zero. Since a_1 defines only a simple scaling of W, it may hence without loss of generality always be fixed by setting $a_1 = 1$.

The derivation of the fourth- and fifth-order DK Hamiltonian requires explicit care of all terms of the innermost unitary transformation U_1, abbreviated in this section as U, up to at most fourth order in W. Consequently, the deviation of U from unitarity is given by

$$UU^\dagger - \mathbf{1} = (-a_3^2 + a_1^3 a_3 - \tfrac{1}{8}a_1^6) W^6 + \frac{1}{2^6} a_1^2 (8a_3 - a_1^3)^2 W^8. \tag{27}$$

This expression will in general be minimal if the first term in parentheses vanishes. As a quadratic expression for a_3 it has two solutions. In order to achieve the smallest deviation of U from unitarity possible at that point, we will prefer the smaller of these two solutions, which reads

$$a_3 = \frac{2-\sqrt{2}}{4} a_1^3 \approx 0.14645\, a_1^3. \tag{28}$$

With this optimum choice of a_3 the deviation of U from unitarity is given by

$$UU^\dagger - \mathbf{1} = \frac{1}{2^6}(2\sqrt{2}-3)^2\, a_1^8\, W^8 \approx 4.59957\cdot 10^{-4}\, a_1^8\, W^8, \tag{29}$$

whose leading order has been reduced to W^8 by the special choice of a_3. Since all other possible unitary parametrizations would feature a leading order of W^6, i.e., they will in general lead to a larger deviation of U from unitarity, we will denote the DK transformation with this best choice of the coefficients as the *optimal* unitary transformation U^{opt}, e.g., U_1^{opt} for the innermost transformation.

Similarly, the sixth- and seventh-order DK approximations require U to be considered at most up to the term of order W^6. Having previously fixed a_3 according to Eq. (28), the transformation U closest to unitarity, i.e., the optimal transformation for application in the DK method is achieved by the choice

$$a_5 = \frac{24-17\sqrt{2}}{2^6}\, a_1^5 \approx -6.50478\cdot 10^{-4}\, a_1^5, \tag{30}$$

which guarantees a unitary transformation U up to terms of leading order W^{10}, i.e.,

$$UU^\dagger - \mathbf{1} = \underbrace{\frac{3}{2^{11}}(181-2^7\sqrt{2})\, a_1^{10}}_{\approx -2.832\cdot 10^{-5}} W^{10} + \underbrace{\frac{1}{2^{12}}(24-17\sqrt{2})^2\, a_1^{12}}_{\approx 4.231\cdot 10^{-7}} W^{12}. \tag{31}$$

The same ideas may be repeatedly applied to derive higher-order terms of the optimal parametrization U^{opt} to be applied in the DK method. This procedure will fix the higher-order odd coefficients a_{2k+1} uniquely. Since these higher-order DK transformations will not be carried out in this work we only briefly give the results for the following two coefficients:

$$\begin{aligned} a_7 &= \frac{3}{2^{11}}(2^8-181\sqrt{2})\, a_1^7 \approx 4.00565\cdot 10^{-5}\, a_1^7, \\ a_9 &= \frac{1}{2^{15}}(3\cdot 2^{12}-8689\sqrt{2})\, a_1^9 \approx -3.10191\cdot 10^{-6}\, a_1^9. \end{aligned} \tag{32}$$

In general, if the power series expansion of U is truncated after the term of order W^k, application of the optimal DK parametrization U^{opt} guarantees that the leading term of $UU^\dagger - \mathbf{1}$ is of order W^{k+4} instead of order W^{k+2} as for all other unitary parametrizations.

The superior performance of the optimal parametrization U^{opt} is also documented by Tables I and II. In Table I, the coefficients a_k of four different parametrizations of U are compared. Both the exponential and the optimal unitary parametrization U^{opt} are rapidly converging. For truncated expansions of U the optimal parametrization behaves significantly better than all other choices for the coefficients a_k, as is clearly demonstrated by the deviations of U from unitarity presented in Table II. Especially for DKH5, i.e., for a truncation of U after the term of fourth-order in W, the operator norm $|UU^\dagger - \mathbf{1}|$ for U^{opt} will be dramatically smaller than for all other parametrizations. It should not be forgotten that the truncation of any power series applied in the DK transformation does necessarily require that the operator norm of W is smaller than 1, since otherwise the higher-order terms in W would dominate the expansion. This leads to an even better performance of the optimal unitary parametrization U^{opt} as compared to all other choices for the coefficients than it is evident by the numerical results in Table II. As a consequence, the eigenvalues of the transformed Hamiltonian $H_{\mathrm{DKHn}} = UH_DU^\dagger$ will be significantly closer to the exact eigenvalues of the Dirac Hamiltonian H_D if the optimal parametrization U^{opt}, instead of any other parametrization, is truncated after a finite number of terms. Obviously, in the limit of considering infinitely many terms of the power series for U these differences will, depending on the chosen parametrization, altogether more or less rapidly tend to zero.

TABLE I. Coefficients a_k of the power series expansion of the unitary transformation U for four different parametrizations. The first two coefficients have been fixed to $a_0 = a_1 = 1$. All coefficients are given with an accuracy of three digits.

	$U=\sqrt{1+W^2}+W$	$U=\frac{2+W}{2-W}$	$U=\exp(W)$	U^{opt}
a_2	5.000E−1	5.000E−1	5.000E−1	5.000E−1
a_3	0	2.500E−1	1.667E−1	1.464E−1
a_4	−1.250E−1	1.250E−1	4.167E−2	2.145E−2
a_5	0	6.250E−2	8.334E−3	−6.505E−4
a_6	6.250E−2	3.125E−2	1.389E−3	−6.505E−4
a_7	0	1.563E−2	1.984E−4	4.006E−5
a_8	−3.906E−2	7.813E−3	2.480E−5	4.006E−5
a_9	0	3.906E−3	2.756E−6	−3.102E−6
a_{10}	2.734E−2	1.953E−3	2.756E−7	−3.102E−6
R_c	1	2	∞	

III. DERIVATION OF THE DK HAMILTONIANS

In this section the sequence of unitary transformations defined in Eq. (14) is set up and the block-diagonal Hamiltonian H_{bd} is constructed step by step. In order to investigate a potential dependence of the DK Hamiltonians H_{DKHn} on the coefficients $a_{i,k}$, we do not restrict the derivation to the optimal parametrization of the transformations U_i derived in the last section, but apply the most general parametrization of U_i with the coefficients $a_{i,k}$ satisfying the unitarity conditions Eqs. (19)–(24) only. The first subscript of the coeffi-

TABLE II. Lowest-order terms of $UU^\dagger - 1$, for given truncation of U after $\mathcal{O}(W^k)$ for four different types of parametrizations. The first two coefficients have been fixed to $a_0 = a_1 = 1$. All values are given with an accuracy of three digits.

k	$U=\sqrt{1+W^2}+W$	$U=\frac{2+W}{2-W}$	$U=\exp(W)$	U^{opt}
4	−1.250E−1 W^6	6.250E−2 W^6	1.389E−2 W^6	4.600E−4 W^8
6	7.813E−2 W^8	1.563E−2 W^8	3.472E−4 W^8	−2.832E−5 W^{10}
8	−5.469E−2 W^{10}	3.906E−3 W^{10}	4.960E−6 W^{10}	2.193E−6 W^{12}
10	4.102E−2 W^{12}	9.766E−4 W^{12}	4.593E−8 W^{12}	−1.908E−7 W^{14}

cients $a_{i,k}$ characterizes the corresponding unitary matrix U_i. For later convenience the odd and antihermitean expansion parameter is denoted by W_i' instead of W_i. Although we have already derived the DK expressions up to fourth order (DKH4),[2] we recall the results here since the DKH5 terms depend on all preceding steps. The transformation of the fpFW Hamiltonian H_1 with U_1 yields

$$\begin{aligned} H_2 = U_1 H_1 U_1^\dagger &= \left[a_{1,0}\mathbf{1} + \sum_{k=1}^{\infty} a_{1,k} W_1'^k \right] (\mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1) \\ &\quad \times \left[a_{1,0}\mathbf{1} + \sum_{k=1}^{\infty} (-1)^k a_{1,k} W_1'^k \right] \\ &= \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1^{(2)} + \mathcal{E}_2 + \mathcal{O}_2^{(2)} + \mathcal{E}_3 \\ &\quad + \mathcal{O}_3^{(2)} + \sum_{k=4}^{\infty} (\mathcal{E}_k^{(2)} + \mathcal{O}_k^{(2)}), \end{aligned} \tag{33}$$

with

$$\mathcal{O}_1^{(2)} = \mathcal{O}_1 + a_{1,0} a_{1,1} [W_1', \mathcal{E}_0], \tag{34}$$

$$\mathcal{E}_2 = a_{1,0} a_{1,1} [W_1', \mathcal{O}_1] + \tfrac{1}{2} a_{1,1}^2 [W_1', [W_1', \mathcal{E}_0]], \tag{35}$$

$$\mathcal{O}_2^{(2)} = a_{1,0} a_{1,1} [W_1', \mathcal{E}_1], \tag{36}$$

$$\mathcal{E}_3 = \tfrac{1}{2} a_{1,1}^2 [W_1', [W_1', \mathcal{E}_1]], \tag{37}$$

$$\begin{aligned} \mathcal{O}_3^{(2)} &= \tfrac{1}{2} a_{1,1}^2 [W_1', [W_1', \mathcal{O}_1]] - \tfrac{1}{2} a_{1,0} a_{1,1}^3 W_1' [W_1', \mathcal{E}_0] W_1' \\ &\quad + a_{1,0} a_{1,3} [W_1'^3, \mathcal{E}_0], \end{aligned} \tag{38}$$

$$\begin{aligned} \mathcal{E}_4^{(2)} &= a_{1,1} a_{1,3} [W_1'^3, [W_1', \mathcal{E}_0]] - \tfrac{1}{8} a_{1,1}^4 [W_1'^2, [W_1'^2, \mathcal{E}_0]] \\ &\quad + a_{1,0} a_{1,3} [W_1'^3, \mathcal{O}_1] - \tfrac{1}{2} a_{1,0} a_{1,1}^3 W_1' [W_1', \mathcal{O}_1] W_1', \end{aligned} \tag{39}$$

$$\begin{aligned} \mathcal{E}_5^{(2)} &= -\tfrac{1}{8} a_{1,1}^4 [W_1'^2, [W_1'^2, \mathcal{E}_1]] \\ &\quad + a_{1,1} a_{1,3} [W_1'^3, [W_1', \mathcal{E}_1]]. \end{aligned} \tag{40}$$

Since this presentation focuses on the fifth-order DK Hamiltonian, only those terms are explicitly given at this first stage, which are required to derive the final fifth-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 such a term belongs to the intermediate, partially transformed Hamiltonian relevant only for the following higher-order terms. Only those even terms, which will not be affected by the succeeding unitary transformations U_i ($i = 2,3,\ldots$) bear no superscript and may already be identified with the corresponding terms in the expansion of H_{bd} given by Eq. (14). 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. Hence, H_{bd} is already defined up to third order in the external potential 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 $W_1', W_2', \ldots, W_n'$, 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:

$$[W_1', \mathcal{E}_0] = -\frac{a_{1,0}}{a_{1,1}} \mathcal{O}_1, \tag{41}$$

which is satisfied if and only if the kernel of W_1' is given by

$$W_1'(i,j) = \frac{a_{1,0}}{a_{1,1}} \beta \frac{\mathcal{O}_1(i,j)}{E_i + E_j}. \tag{42}$$

This choice of W_1' satisfies all constraints, namely that it is an odd and antihermitean operator of first order in V. Note that W_1' depends on the beforehand arbitrarily chosen coefficients $a_{1,0}$ and $a_{1,1}$, i.e., it is linear in $a_{1,0}/a_{1,1}$. We therefore introduce the modified operator W_1 defined by

$$W_1(i,j) = a_{1,0} a_{1,1} W_1'(i,j) = \beta \frac{\mathcal{O}_1(i,j)}{E_i + E_j}, \tag{43}$$

which is manifestly independent of the coefficients $a_{1,k}$. With this choice of W_1 and by utilizing relation (41) the above results may be simplified to a large extent,

$$\mathcal{E}_2 = \tfrac{1}{2} [W_1, \mathcal{O}_1], \tag{44}$$

$$\mathcal{O}_2^{(2)} = [W_1, \mathcal{E}_1], \tag{45}$$

$$\mathcal{E}_3 = \tfrac{1}{2} [W_1, [W_1, \mathcal{E}_1]], \tag{46}$$

$$\mathcal{O}_3^{(2)} = \tfrac{1}{2} [W_1, [W_1, \mathcal{O}_1]] + \tfrac{1}{2} W_1 \mathcal{O}_1 W_1 + \frac{a_{1,3}}{a_{1,1}^3} [W_1^3, \mathcal{E}_0], \tag{47}$$

$$\mathcal{E}_4^{(2)} = \tfrac{1}{8} [W_1, [W_1, [W_1, \mathcal{O}_1]]], \tag{48}$$

$$\mathcal{E}_5^{(2)} = -\tfrac{1}{8} [W_1^2, [W_1^2, \mathcal{E}_1]] + \frac{a_{1,3}}{a_{1,1}^3} [W_1^3, [W_1, \mathcal{E}_1]]. \tag{49}$$

We find that all terms contributing to the fourth-order DK Hamiltonian H_{DKH4} are independent of the coefficients $a_{1,k}$, i.e., they are invariant under an arbitrary change of the parametrization of U_1. Terms contributing to the fifth- and higher-order DK corrections, however, depend on the parametrization of U_1. The next unitary transformation U_2 is applied in order to eliminate the odd term of second order,

$$\begin{aligned} H_3 = U_2 H_2 U_2^\dagger &= \left[a_{2,0}\mathbf{1} + \sum_{k=1}^{\infty} a_{2,k} W_2'^k \right] \\ &\quad \times H_2 \left[a_{2,0}\mathbf{1} + \sum_{k=1}^{\infty} (-1)^k a_{2,k} W_2'^k \right] \\ &= \sum_{k=0}^{5} \mathcal{E}_k + \sum_{k=6}^{\infty} \mathcal{E}_k^{(3)} + \sum_{k=2}^{\infty} \mathcal{O}_k^{(3)} \end{aligned} \tag{50}$$

with

$$\mathcal{O}_2^{(3)} = \mathcal{O}_2^{(2)} + a_{2,0}a_{2,1}[W_2', \mathcal{E}_0], \tag{51}$$

$$\mathcal{E}_4 = \mathcal{E}_4^{(2)} + a_{2,0}a_{2,1}[W_2', \mathcal{O}_2^{(2)}] + \tfrac{1}{2}a_{2,1}^2[W_2', [W_2', \mathcal{E}_0]], \tag{52}$$

$$\mathcal{E}_5 = \mathcal{E}_5^{(2)} + a_{2,0}a_{2,1}[W_2', \mathcal{O}_3^{(2)}] + \tfrac{1}{2}a_{2,1}^2[W_2', [W_2', \mathcal{E}_1]]. \tag{53}$$

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,

$$[W_2', \mathcal{E}_0] = -\frac{a_{2,0}}{a_{2,1}}\mathcal{O}_2^{(2)} = -\frac{a_{2,0}}{a_{2,1}}[W_1, \mathcal{E}_1]. \tag{54}$$

After introduction of the modified operator $W_2 = a_{2,0}a_{2,1}W_2'$, this is guaranteed if and only if the kernel of W_2 is given by

$$W_2(i,j,k) = \beta\frac{W_1(i,j)\mathcal{E}_1(j,k) - \mathcal{E}_1(i,j)W_1(j,k)}{E_i + E_k}. \tag{55}$$

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 independent of the chosen parametrizations of the unitary transformations. W_2 is thus a second-order integral operator in momentum space, whose action on a 4-spinor ϕ is defined by

$$W_2\,\phi(\boldsymbol{p}_i) = \int \frac{\mathrm{d}^3\boldsymbol{p}_j \mathrm{d}^3\boldsymbol{p}_k}{(2\pi\hbar)^6} W_2(\boldsymbol{p}_i, \boldsymbol{p}_j, \boldsymbol{p}_k)\,\phi(\boldsymbol{p}_k) = f(\boldsymbol{p}_i). \tag{56}$$

With this choice of W_2 the final results for the fourth- and fifth-order even terms are given by

$$\mathcal{E}_4 = \tfrac{1}{8}[W_1, [W_1, [W_1, \mathcal{O}_1]]] + \tfrac{1}{2}[W_2, [W_1, \mathcal{E}_1]], \tag{57}$$

$$\mathcal{E}_5 = \tfrac{1}{2}[W_2, [W_2, \mathcal{E}_1]] + \tfrac{1}{2}[W_2, [W_1, [W_1, \mathcal{O}_1]]] + \tfrac{1}{2}[W_2, W_1\mathcal{O}_1W_1] + -\tfrac{1}{8}[W_1^2, [W_1^2, \mathcal{E}_1]] + \frac{a_{1,3}}{a_{1,1}^3}[[W_2, W_1^3], \mathcal{E}_0], \tag{58}$$

where we have extensively taken advantage of Eq. (54) in order to simplify the expressions. It should be mentioned that earlier Nakajima and Hirao have already tried to derive the formulas for both the kernel of W_2, Eq. (55), and the fourth- and fifth-order Hamiltonians, Eqs. (57) and (58), employing the exponential parametrization of the unitary matrices.[31] However, they have not yet given any numerical results for the fourth- and fifth-order DK correction. Furthermore, their expressions contain some misprints and are based on the exponential instead of the most general parametrization of the unitary matrices.

While the term $\mathcal{E}_4$ is still independent of the chosen parametrizations of the two unitary transformations,[2] the subsequent even term $\mathcal{E}_5$ depends on the coefficients $a_{1,1}$ and $a_{1,3}$ of the parametrization of the first DK transformation U_1. We will therefore fix the coefficient $a_{1,3}$ according to Eq. (28) of the discussion in Sec. II. This procedure guarantees that the eigenvalues of H_{DKH5} will deviate as little as possible from the exact eigenvalues of H_D, as we have described in detail in the last section.

The electronic, i.e., upper-left (2×2)-blocks of the kernels of the lowest order terms may be explicitly given as

$$\mathcal{E}_{0+}(i) = E_i - mc^2, \tag{59}$$

$$\mathcal{E}_{1+}(i,j) = \underbrace{A_i(V_{ij} + \boldsymbol{P}_iV_{ij}\boldsymbol{P}_j)A_j}_{\mathcal{E}_{1+}^{\mathrm{sf}}(i,j)} + \underbrace{\mathrm{i}A_i\,\boldsymbol{\sigma}\cdot(\boldsymbol{P}_i\times V_{ij}\boldsymbol{P}_j)A_j}_{\mathcal{E}_{1+}^{\mathrm{sd}}(i,j)}, \tag{60}$$

$$\begin{aligned}\mathcal{E}_{2+}(i,j,k) = \tfrac{1}{2}\{&-A_i\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_i\,\tilde{V}_{ij}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_jA_j\,A_jV_{jk}A_k + A_i\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_i\,\tilde{V}_{ij}A_j\,A_jV_{jk}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_k\,A_k + A_i\tilde{V}_{ij}A_j\,P_j^2\,A_jV_{jk}A_k\\ &- A_i\tilde{V}_{ij}A_j\,A_j\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_jV_{jk}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_k\,A_k - A_i\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_i\,V_{ij}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_jA_j\,A_j\tilde{V}_{jk}A_k\\ &+ A_i\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_i\,V_{ij}A_j\,A_j\tilde{V}_{jk}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_k\,A_k + A_iV_{ij}A_j\,P_j^2\,A_j\tilde{V}_{jk}A_k - A_iV_{ij}A_j\,A_j\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_j\,\tilde{V}_{jk}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_k\,A_k\},\end{aligned} \tag{61}$$

$$\mathcal{E}_{3+}(i,j,k,l) = \tfrac{1}{2}\{A_i\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_i\,\tilde{V}_{ij}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_j\,A_j\,A_j\tilde{V}_{jk}A_k\,\mathcal{E}_1(k,l) + \cdots, \tag{62}$$

where the abbreviation

$$\tilde{V}_{ij} = \frac{V_{ij}}{E_i + E_j} = \frac{V(\boldsymbol{p}_i, \boldsymbol{p}_j)}{\sqrt{\boldsymbol{p}_i^2c^2 + m^2c^4} + \sqrt{\boldsymbol{p}_j^2c^2 + m^2c^4}} \tag{63}$$

has been introduced. Furthermore, Dirac's relation

$$\boldsymbol{\sigma}\cdot\boldsymbol{P}_i\,V_{ij}\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_j = \boldsymbol{P}_i\cdot V_{ij}\boldsymbol{P}_j + \mathrm{i}\,\boldsymbol{\sigma}\cdot(\boldsymbol{P}_i\times V_{ij}\boldsymbol{P}_j) \tag{64}$$

for Pauli spin matrices has been used, which, in the case of vanishing potential, simplifies to

$$\boldsymbol{\sigma}\cdot\boldsymbol{P}_j\,\boldsymbol{\sigma}\cdot\boldsymbol{P}_j = P_j^2. \tag{65}$$

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 $\mathcal{E}_3$, $\mathcal{E}_4$, and $\mathcal{E}_5$ given by Eqs. (46), (57), and (58) with the help of Eqs. (10), (11), (43), and (55).

IV. RESULTS

The numerical performance of the generalized DK transformation up to fifth order is investigated for both hydrogenlike ions and many-electron atomic systems. The scalar-relativistic Hamiltonians H_{DKH1} up to H_{DKH5} have been implemented into an atomic Hartree–Fock program based on the work by Roothaan and Bagus.[32] The DK transformation was only applied to the one-electron terms of the Hamil-

TABLE III. Ground state 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 (Ref. 33) with originally 32 s-functions, augmented up to 50 s-functions for systems with high nuclear charge. The speed of light $c=137.035\,989\,5$ was used for all calculations (Ref. 34).

Z	20	40	60	80	100	120
n.r.	−199.999 984	−799.999 988	−1 799.999 97	−3 199.999 91	−4 999.999 8	−7 199.999 5
DKH1	−201.341 494	−823.894 221	−1 934.202 84	−3 686.448 68	−6 472.402 6	−12 132.679 9
DKH2	−201.072 538	−817.615 772	−1 893.897 64	−3 523.324 84	−5 906.191 8	−9 594.096 0
DKH3	−201.076 660	−817.820 110	−1 895.844 04	−3 533.119 56	−5 942.369 4	−9 712.931 1
DKH4	−201.076 508	−817.804 850	−1 895.627 02	−3 531.708 56	−5 936.473 9	−9 698.523 5
DKH5	−201.076 523	−817.808 095	−1 895.702 82	−3 532.461 47	−5 941.528 5	−9 730.968 4
DEQ[a]	−201.076 523	−817.807 498	−1 895.682 36	−3 532.192 15	−5 939.195 4	−9 710.783 5

[a]Analytical value according to the Dirac equation, see Eq. (66).

tonian and the nonrelativistic two-electron Coulomb repulsion terms remained unchanged. For all calculations we have employed the uncontracted relativistic universal Gaussian basis set provided by Malli *et al.*,[33] comprising 32 even-tempered exponents. The value for the speed of light $c=137.035\,989\,5$ was taken from Ref. 34.

A. One-electron systems

The numerical accuracy and basic features of the various DK approximations are investigated. Therefore, the ground state, i.e., $1s$ energies of hydrogenlike ions for the whole periodic table are determined for the nonrelativistic (n.r.) case as well as for the various Douglas–Kroll (DKHn) Hamiltonians. Since these systems feature only one single electron in an s-orbital, no inaccuracy is introduced by the neglect of the spin-dependent terms and of the DK transformation of the two-electron terms. A point-nucleus model was applied in order to compare the results to the analytically known exact eigenvalues resulting from the Dirac equation (DEQ), which are given by

$$E_{1s_{1/2}}=mc^2(\sqrt{1-(Z\alpha)^2}-1), \tag{66}$$

where α is the fine structure constant. The smallest exponent of the universal Gaussian basis set is given by 0.021 494. In order to achieve sufficiently high accuracy to resolve the higher-order DK corrections properly even for systems with very large nuclear charge Z, we have augmented this basis with 18 additional large exponents. The ratio between two subsequent additional exponents we have added is 2.054 433, according to the even-tempered ratio derived from the original exponents of Malli *et al.*[33] The resulting basis set contained 50 s-functions and exponents up to 10^{14}. The numerical results for six exemplary systems with increasing nuclear charge are shown in Table III.

The exact nonrelativistic result was recovered for all calculations to very high accuracy. The very small deviation of at most 10^{-6}% proves that the basis set chosen is able to describe the wave function close to the nucleus very well, at least for the nonrelativistic description based on the Schrödinger equation. DKH2 represents a significant improvement over the nonrelativistic result for all values of the nuclear charge Z, whereas the first-order DK correction dramatically overestimates the binding energy, as it is well known for a long time.[35] Due to this huge over-binding the first-order DK approximation does not have any practical value. For increasing values of Z, however, also DKH2 does no longer describe the relativistic effects on the *total* energy appropriately, as, e.g., already for $Z=100$ the absolute error is about 33 hartrees, increasing rapidly up to about 137 hartrees for $Z=120$. For those highly relativistic systems higher-order approximations are important and, indeed, the results obtained with DKH3, DKH4, and DKH5 are in much better agreement with the exact Dirac eigenvalues. One necessarily has to go beyond the established second-order DK method for highly accurate total energies of systems including heavy nuclei. Fortunately, the third- and fourth-order corrections DKH3 and DKH4 do already remove the major part of the deficiencies of the second-order approximation.

There is one further subtlety connected with higher-order DK transformations one should be aware of. The energies obtained with odd DK corrections, i.e., DKH1, DKH3, and DKH5 are always below the exact Dirac eigenvalues, which is demonstrated by Table III. This indicates clearly that

TABLE IV. Ground state energies for hydrogenlike systems with high nuclear charge Z for three different basis sets in Hartree atomic units. See text for further details. The speed of light $c=137.035\,989\,5$ was used for all calculations (Ref. 34).

	32 exponents			41 exponents			50 exponents		
Z	100	110	120	100	110	120	100	110	120
DKH1	−6461.94	−8554.97	−11638.82	−6472.07	−8609.99	−12041.41	−6472.40	−8613.85	−12132.68
DKH2	−5905.26	−7513.94	−9569.10	−5906.18	−7518.39	−9593.20	−5906.19	−7518.46	−9594.10
DKH3	−5940.92	−7578.06	−9682.54	−5942.36	−7584.09	−9712.07	−5942.37	−7584.16	−9712.93
DKH4	−5935.12	−7567.66	−9665.80	−5936.46	−7573.69	−9697.12	−5936.47	−7573.82	−9698.52
DKH5	−5939.63	−7578.09	−9689.30	−5941.50	−7586.09	−9728.78	−5941.53	−7586.31	−9730.97
DEQ[a]	−5939.20	−7579.69	−9710.78	−5939.20	−7579.69	−9710.78	−5939.20	−7579.69	−9710.78

[a]Analytical value according to the Dirac equation, see Eq. (66).

TABLE V. Ground state energies for the silver atom and cation in Hartree atomic units. For all calculations a $32s29p20d$ universal Gaussian basis set (Ref. 33) was used (see text for details). All energy differences $\Delta E = E_{\mathrm{DKH}n} - E_{\mathrm{DFC}}$ refer to the 4-component DFC values. The ionization energy was calculated as $\mathrm{IE} = E(\mathrm{Ag}^+) - E(\mathrm{Ag}^0)$. The speed of light $c = 137.035\,989\,5$ was used for all calculations (Ref. 34).

	Ag^0			Ag^+		
	E	ΔE	$\varepsilon_{\mathrm{HOMO}}$[a]	E	ΔE	IE
n.r.	−5197.6980	+117.04	−0.2120	−5197.4809	+117.03	0.2171
DKH1	−5340.6559	−25.915	−0.2394	−5340.4206	−25.913	0.2353
DKH2	−5311.8945	+2.8459	−0.2368	−5311.6617	+2.8456	0.2328
DKH3	−5312.9985	+1.7419	−0.2369	−5312.7656	+1.7417	0.2329
DKH4	−5312.9019	+1.8385	−0.2369	−5312.6689	+1.8384	0.2329
DKH5	−5312.9263	+1.8141	−0.2369	−5312.6934	+1.8139	0.2329
DFC[b]	−5314.7404	±0.0000	−0.2372	−5314.5073	±0.0000	0.2331

[a]Orbital energy of the highest occupied orbital, i.e., the $5s$-orbital for Ag^0.
[b]4-component DFC results obtained with MOLFDIR (Ref. 36).

H_{DKH3} and H_{DKH5} are only variationally stable but not variational approximations to the exact electronic Hamiltonian. However, an extension of the DK method to the next even order in the external potential does always cure this deficiency of the odd DK approximations. The binding energies calculated with h_+ derived from DKH4 are always found to be above the corresponding Dirac values, supporting the conjecture that DKH4 is a variational method. The overestimation of the $1s$ binding energy is a very important feature of DKH3 that has not yet been observed in the only earlier study about the third-order DK method.[31] It is only revealed by application 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 ions.

The necessity for sufficiently large basis sets in order to resolve DK corrections for highly charged systems properly is documented in Table IV. Only large basis sets with more than 40 exponents yield correct DK energies and reproduce the above mentioned features of the DK transformation. Our smallest basis with 32 exponents is not able to reveal the overbinding of the odd DK Hamiltonians. Furthermore, all energies obtained with this small basis set are significantly too small in absolute value, i.e., too positive, since one is far away from the basis set limit.

For systems with nuclear charge Z greater than 104 we find the DKH5 energy always to be below the result obtained with DKH3. This could possibly indicate a divergence behavior of the higher-order DKH corrections. However, it is most likely that even our largest basis with 50 exponents is not suitable to model the region close to the nucleus in the presence of very strong electric fields as it is the case for these highly-charged heavy ions. We should note that this deficiency is only of minor importance for chemical purposes, where we usually deal with neutral or weakly-charged systems.

B. Many-electron atoms

Tables V and VI show the results of calculations on the silver and gold atom for the nonrelativistic case as well as for the various DK approximations and the DFC Hamiltonian. We used a $32s29p20d15f$ uncontracted universal Gaussian basis set for all calculations.[33] For the neutral silver and gold atoms the ^2S ground state configuration, i.e., $[\mathrm{Kr}]4d^{10}5s^1$ for Ag^0 and $[\mathrm{Xe}]5d^{10}6s^1$ for Au^0 was investigated. The closed-shell cations Ag^+ and Au^+ were obtained by removing the highest s-orbital electron.

All 4-component DFC calculations were performed with MOLFDIR.[36] Since MOLFDIR employs a Gaussian nuclear model, we have described the desired pointlike nucleus by increasing the exponent for the Gaussian nuclear charge distribution to 10^{20}. A comparison of our calculated DFC results for the neutral atoms with the numerical 4-component DFC benchmark results for point nuclei provided by Visscher and Dyall[37] revealed only an insignificant error of the order of the error introduced by the limited size of the basis set. The deficiency of the latter was found to be smaller than 0.003 a.u. ($<10^{-4}$%) for silver and 0.259 a.u. ($<10^{-3}$%) for gold.

For both atoms the nonrelativistic total energy E is

TABLE VI. Ground state energies for the gold atom and cation in Hartree atomic units. For all calculations a $32s29p20d15f$ universal Gaussian basis set (Ref. 33) was used (see text for details). The same symbols and conventions are employed as in Table V.

	Au^0			Au^+		
	E	ΔE	$\varepsilon_{\mathrm{HOMO}}$	E	ΔE	IE
n.r.	−17 865.394 4	+1174.19	−0.2208	−17 865.177 0	−1174.13	0.2174
DKH1	−19 339.308 8	−299.723	−0.3061	−19 339.012 9	−299.710	0.2959
DKH2	−18 993.722 1	+45.8635	−0.2894	−18 993.441 6	−45.8612	0.2805
DKH3	−19 014.295 2	+25.2904	−0.2904	−19 014.013 8	−25.2890	0.2814
DKH4	−19 011.347 3	+28.2383	−0.2903	−19 011.066 0	−28.2368	0.2813
DKH5	−19 012.810 3	+26.7753	−0.2904	−19 012.528 9	−26.7739	0.2814
DFC	−19 039.585 6	±0.00000	−0.2919	−19 039.302 8	±0.00000	0.2828

found to deviate sizeably from the exact, i.e., 4-component DFC values. An application of the DK approximation up to third order significantly improves on the total energy. A further extension of the DK transformation to fourth and fifth order yields only minor contributions. The order of magnitude of these higher order corrections, i.e., the changes between DKH3 and DKHn ($n=4,5$), are 0.1 a.u. for silver and 3 a.u. for gold. These changes are smaller than the effect of the DK transformation of the two-electron terms, which was earlier found to be about 1.1 a.u. for silver and 6.5 a.u. for gold.[38] It seems thus necessary to take care of both the DK transformation of the two-electron terms and the spin-dependent terms that were neglected in this implementation before extending the scalar-relativistic DK transformation of the one-electron terms to higher orders. Furthermore, due to the previously discussed over-binding of the third-order DK correction, DKH3 does always yield the best approximation to the exact total energy. It is therefore recommendable to prefer DKH3 instead of the standard DKH2 variant for relativistic many-electron calculations of quantum chemistry.

The same conclusion may be drawn by an investigation of the dependence of relative energies like the ionization energy $\mathrm{IE}=E(X^+)-E(X^0)$ ($X=\mathrm{Ag}$, Au) and the energy of the highest occupied orbital $\varepsilon_{\mathrm{HOMO}}$ on the order of the DK transformation. Both IE and $\varepsilon_{\mathrm{HOMO}}$ change significantly up to DKH3, but are almost unchanged by transition to DKH4 and DKH5. Again, the deviation of the DKH ionization energy from the DFC value is due to the neglect of the spin-dependent terms and the DK transformation of the two-electron terms.

It should be mentioned that our calculated results have necessarily been compared to the 4-component DFC values, and not to experimental values. Both our Hartree–Fock DK and the relativistically analogous Dirac–Fock SCF calculations do not include any electron–electron correlation effects except exchange. By contrast, the deviation of our results from the experimental values is mainly due to the neglect of correlation effects. However, our Hartree–Fock-type calculations represent a test of the methodology rather than a comparison with experiment.

The estimate of the ionization energy via Koopmans' theorem $\mathrm{IE}=-\varepsilon_{\mathrm{HOMO}}$ approaches the experimental values with slightly higher accuracy than our ΔSCF calculations. This is due to the well-known effect of the neglect of the orbital relaxation, which partially compensates the error introduced by the neglect of correlation effects.

The results of Tables V and VI indicate clearly, that a scalar-relativistic implementation of the one-electron DK transformation up to any order is insufficient for highly accurate calculations of the relativistic effects on the total energy. However, for most chemical applications relative energies and properties, for which already DKH3 yields very satisfactory results, are by far more important.

V. CONCLUSION

We have derived the most general parametrization of the unitary matrices U_i applied in the DK transformation sequence. It is given as a power series expansion in an odd and anti-Hermitian operator W_i of ith order in the external potential. The only constraints are the unitarity conditions for the even coefficients of this power series. In particular, the traditional square root parametrization introduced by Douglas and Kroll, $U_i=\sqrt{1+W_i^2}+W_i$, is only one special case of infinitely many equivalent possibilities.

In practical applications one always has to truncate the power series expansion for U_i after some finite number of terms, depending on the order of the DK approximation sought for. However, due to W_i being an ith-order operator in the external potential, it is mandatory to expand the innermost unitary transformations to higher order in W_i than the outer transformations. For example, the consistent derivation of H_{DKH5} requires U_1 to be expanded up to terms of order W_1^4, but U_2 only up to terms of W_2^2.

These truncations of the power series expansions of U_i lead to deviations from unitarity, which depend on the chosen parametrization. In order to minimize these errors, we derived the coefficients of the optimal parametrization U^{opt}, which is still closest to unitarity if it is truncated after any arbitrary order in W_i. In general, if the power series expansion of U_i is truncated after the term of order W_i^k, application of the optimal DK parametrization U_i^{opt} guarantees that the leading term of $U_iU_i^\dagger-\mathbf{1}$ is of order W_i^{k+4} instead of order W_i^{k+2} as for all other unitary parametrizations.

Applying the most general parametrization for U_i, we found the DK Hamiltonians up to DKH4 to be independent on the chosen parametrizations of the unitary transformations U_i. The fifth- and all higher-order Hamiltonians, however, depend on the choice of the coefficients of the power series parametrizations. This arbitrariness in the DK Hamiltonians vanishes consistently by application of U^{opt}, leading to eigenvalues of the transformed DK Hamiltonians that are as close as possible to the ones of the original Dirac Hamiltonian.

The DK method features excellent convergence behavior since the nth-order kernel contains $n-1$ factors of $\tilde{V}$ defined by Eq. (63), i.e., it is damped by a factor smaller than $(2mc^2)^{-n+1}$. An extension of this generalized Douglas–Kroll transformation to sixth and higher order in the external potential is straightforward, but will yield only tiny corrections as compared to DKH5. Furthermore, before extending the DK procedure to higher than third order in the external potential, it is more important to previously consider the spin-dependent terms and the DK transformation of the two-electron terms of the many-particle Hamiltonian. 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 most likely, in general, not lead to significant changes on relative energies and properties.

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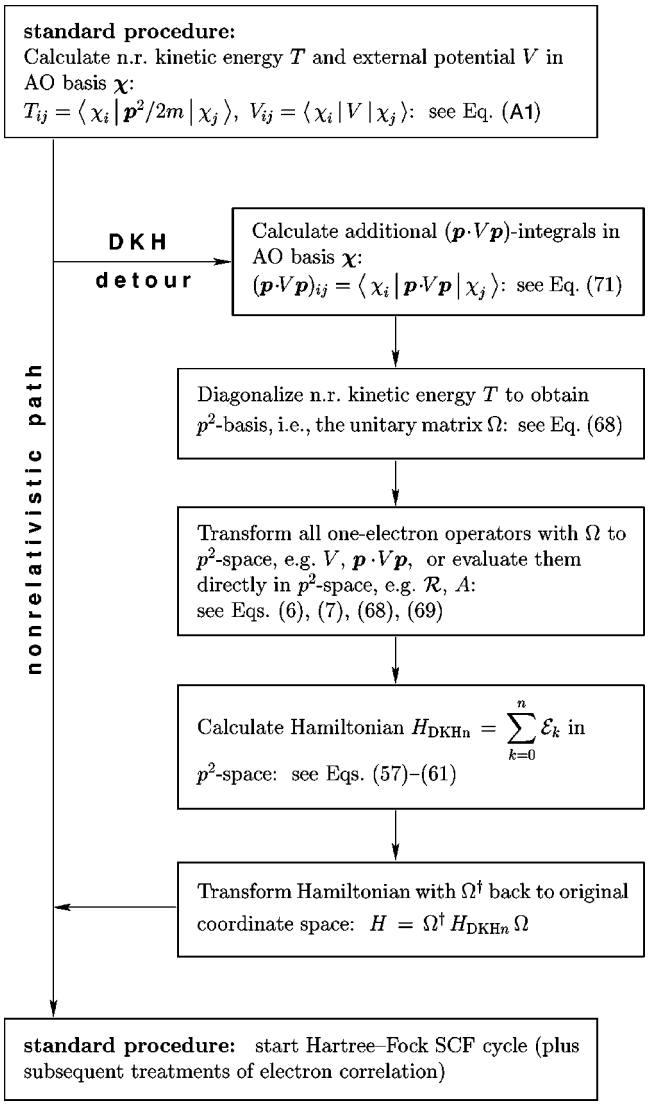

FIG. 1. Diagrammatic presentation of the implementation of the DK transformation of the one-electron terms into *standard* quantum chemical programs. See text for detailed description.

APPENDIX: COMPUTATIONAL DETAILS AND IMPLEMENTATION

In order to provide all necessary information on the computational methodology, the implementation of the DK transformation is briefly discussed. It is certainly one of the greatest advantages of the DK transformation that its spin-free variant can be implemented into every nonrelativistic 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 (see Fig. 1 for a data flow diagram).

The nonrelativistic electronic Hamiltonian H for a molecular system made up of N electrons and M nuclei is in Born–Oppenheimer approximation given by

$$H = \underbrace{\frac{1}{2}\sum_{\substack{\mu,\nu=1\\ \mu\neq\nu}}^{M}\frac{Z_\mu Z_\nu e^2}{|\boldsymbol{R}_\mu-\boldsymbol{R}_\nu|}}_{H_0} + \underbrace{\sum_{i=1}^{N}\frac{\boldsymbol{p}_i^2}{2m}}_{T} + \underbrace{\sum_{i=1}^{N}\sum_{\mu=1}^{M}\frac{-Z_\mu e^2}{|\boldsymbol{r}_i-\boldsymbol{R}_\mu|}}_{V} + \underbrace{\frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\frac{e^2}{|\boldsymbol{r}_i-\boldsymbol{r}_j|}}_{H_2}, \tag{A1}$$

and contains zero-, one-, and two-electron terms. Only the one-electron terms of the kinetic energy T and the electron-nucleus interaction potential V are affected by the DK transformation presented here. Especially the two-electron terms of the electron–electron repulsion potential H_2 remain unchanged.

The natural formulation of the DK transformation, as presented in this work, is given in momentum space, which emerges out of the standard coordinate space formulation by a Fourier transformation. The basic feature of a momentum space formulation is the diagonal form of every function of the momentum $\boldsymbol{p}$, i.e., after introduction of a basis it has a diagonal matrix representation. However, the general DK Hamiltonian H_{DKHn} contains only terms which are functions of the quadratic momentum operator p^2 [see Eqs. (59)–(64)]. 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 Ω can easily be accomplished within every quantum chemical basis set program, where the matrix representation of the nonrelativistic kinetic energy $T=p^2/2m$ is already available. The desired matrix representation of Ω can then be obtained by a diagonalization of T, i.e.,

$$T' = \Omega\, T\, \Omega^\dagger = (t_i)_{i=1,\ldots,n}, \tag{A2}$$

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 $\boldsymbol{\chi}=\{\chi_i:\mathbb{R}^3\rightarrow\mathbb{C}, i=1,\ldots,n\}$. As soon as the unitary matrix Ω is known, it may be applied to all one-electron operators in order to transform them to their p^2-representation. As a consequence, this new matrix representation is diagonal for all functions of p^2, and they may easily be evaluated. For example, the diagonal entries of the $\mathcal{R}$-factors defined by Eq. (7) are given by

$$\mathcal{R}_{p_i} = \mathcal{R}_i = \frac{c}{E_{p_i}+mc^2} = \frac{c}{\sqrt{2mt_ic^2+m^2c^4}+mc^2}. \tag{A3}$$

The A-factors and the relativistic energy–momentum relation given by Eq. (6) are diagonal in p^2-space as well.

After these preliminaries the desired DK Hamiltonian,

$$H_{\mathrm{DKHn}} = \sum_{k=0}^{n}\mathcal{E}_k \tag{A4}$$

may be evaluated. For this purpose the nonrelativistic kinetic energy T has to be simply replaced by the relativistic kinetic

term $\mathcal{E}_0$ given by Eq. (59). Its calculation is straightforward, since it is a diagonal and spin-free, and hence one-component expression. The evaluation of the first-order DK correction $\mathcal{E}_1$ given by Eq. (60) is slightly more complicated, since it requires knowledge of the operator $\boldsymbol{PVP}$. Its matrix elements may, however, be reduced to the representation of the external potential via the relation

$$\langle \chi_i | \boldsymbol{p} \cdot V \boldsymbol{p} | \chi_j \rangle = \hbar^2 \langle \nabla \chi_i | V | \nabla \chi_j \rangle. \tag{A5}$$

These are the only new types of integrals which have to be provided for scalar implementations of the DK procedure, where all spin-dependent terms, e.g., $\mathcal{E}_{1+}^{\mathrm{sd}}$, have simply been neglected.

The essential step in the evaluation of all higher DK corrections is to insert the resolution of the identity,

$$1 = \boldsymbol{\sigma} \cdot \boldsymbol{P}_j \frac{1}{P_j^2} \boldsymbol{\sigma} \cdot \boldsymbol{P}_j, \tag{A6}$$

wherever terms of the structure $\boldsymbol{\sigma} \cdot \boldsymbol{P} V \cdots V \boldsymbol{\sigma} \cdot \boldsymbol{P}$ 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. Again, after subsequent restriction to scalar, i.e., spin-free terms by application of Dirac's relation for Pauli spin matrices given in Eq. (64), the kernels of $\mathcal{E}_k$ contain only computationally feasible terms (see Ref. 2).

Now the spin-free 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. As soon as H_{DKHn} has been evaluated within the chosen p^2-representation, it can be transformed back to the original coordinate space representation by applying the inverse transformation $\Omega^\dagger$. This Hamiltonian is then available for every variational procedure without any further modifications.

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