

Exact decoupling of the Dirac Hamiltonian. II. The generalized Douglas–Kroll–Hess transformation up to arbitrary order

Markus Reiher and Alexander Wolf

Citation: *J. Chem. Phys.* **121**, 10945 (2004); doi: 10.1063/1.1818681

View online: <http://dx.doi.org/10.1063/1.1818681>

View Table of Contents: <http://jcp.aip.org/resource/1/JCPSA6/v121/i22>

Published by the [American Institute of Physics](#).

Additional information on J. Chem. Phys.

Journal Homepage: <http://jcp.aip.org/>

Journal Information: http://jcp.aip.org/about/about_the_journal

Top downloads: http://jcp.aip.org/features/most_downloaded

Information for Authors: <http://jcp.aip.org/authors>

ADVERTISEMENT



**ALL THE PHYSICS
OUTSIDE OF
YOUR JOURNALS.**

www.physicstoday.org
**physics
today**

Exact decoupling of the Dirac Hamiltonian. II. The generalized Douglas–Kroll–Hess transformation up to arbitrary order^{a)}

Markus Reiher^{b)} and Alexander Wolf^{b)}

Lehrstuhl für Theoretische Chemie, Universität Bonn, Wegelerstraße 12, D-53115 Bonn, Germany

(Received 30 August 2004; accepted 27 September 2004)

In order to achieve exact decoupling of the Dirac Hamiltonian within a unitary transformation scheme, we have discussed in part I of this series that either a purely numerical iterative technique (the Barysz–Sadlej–Snijders method) or a stepwise analytic approach (the Douglas–Kroll–Hess method) are possible. For the evaluation of Douglas–Kroll–Hess Hamiltonians up to a pre-defined order it was shown that a symbolic scheme has to be employed. In this work, an algorithm for this analytic derivation of Douglas–Kroll–Hess Hamiltonians up to any arbitrary order in the external potential is presented. We discuss how an estimate for the necessary order for exact decoupling (within machine precision) for a given system can be determined from the convergence behavior of the Douglas–Kroll–Hess expansion prior to a quantum chemical calculation. Once this maximum order has been accomplished, the spectrum of the positive-energy part of the decoupled Hamiltonian, e.g., for electronic bound states, cannot be distinguished from the corresponding part of the spectrum of the Dirac operator. An efficient scalar-relativistic implementation of the symbolic operations for the evaluation of the positive-energy part of the block-diagonal Hamiltonian is presented, and its accuracy is tested for ground-state energies of one-electron ions over the whole periodic table. Furthermore, the first many-electron calculations employing sixth up to fourteenth order DKH Hamiltonians are presented. © 2004 American Institute of Physics.
[DOI: 10.1063/1.1818681]

I. INTRODUCTION

For a consistent (quasi-)relativistic electrons-only theory based on the first-quantized Dirac Hamiltonian, it is desirable to eliminate the unphysical negative-energy states at energies below $-2mc^2$ from the theoretical description. Consequently, one arrives at a computationally less demanding representation for the electronic bound states which does not make any reference to the so-called “small component” (cf. part I¹ for a detailed discussion). Such a two-component relativistic scheme results after complete decoupling of the Dirac Hamiltonian H_D via a suitably chosen unitary transformation U

$$H_{bd} = UH_DU^\dagger = \begin{pmatrix} h_+ & 0 \\ 0 & h_- \end{pmatrix}. \quad (1)$$

The block-diagonal Dirac Hamiltonian H_{bd} possesses exactly the same spectrum as the original Hamiltonian H_D . However, this exact one-step decoupling for Coulombic systems is only possible purely numerically in the framework of the Barysz–Sadlej–Snijders (BSS) method,^{2–4} which does not yield analytic closed-form expressions for the operators. From this BSS approach the infinite-order two-component (IOTC) method of Barysz and collaborators evolved (see, e.g., the recent paper by Kędziera and Barysz⁵). Note, however, that we have used both acronyms (BSS and IOTC) synonymously when referring to this method.

In part I¹ of this series, we have shown that the Douglas–Kroll–Hess (DKH) method^{6–8} is the *only* valid expansion scheme for the decoupled Dirac operator H_{bd} based on unitary transformations

$$H_{bd} = \sum_{k=0}^{\infty} \mathcal{E}_k, \quad (2)$$

that yields analytic closed-form operators. These operators are given through regular and well-defined expressions, and each term \mathcal{E}_k can be classified according to its order in the external potential, which is encoded in the subscript of each term. Actually, the true expansion parameter of the DKH protocol is the scaled or damped external potential \tilde{V} , since each term contributing to \mathcal{E}_k contains exactly $k-1$ factors of \tilde{V} (see below). Moreover, we have argued¹ that it is in principle not possible to carry out *stepwise* decoupling within any two- (or one-) component scheme purely numerically in a recursive manner. Instead, if explicit reference to the small component shall be avoided (and this is always the case in a two- or one-component theory), the DKH operators of ascending order in \tilde{V} can *only* be derived via symbolic operations. Once all these decoupled (even) operators \mathcal{E}_k are derived, they can subsequently be evaluated by transition to a p^2 -basis, i.e., the basis-set representation which diagonalizes the nonrelativistic kinetic energy.⁶

The DKH n Hamiltonians

$$H_{\text{DKH}n} = \sum_{k=0}^n \mathcal{E}_k, \quad (3)$$

^{a)}In memoriam Professor Dr. Bernd Artur Hess.

^{b)}Authors to whom correspondence should be addressed. Electronic mail: reiher@thch.uni-bonn.de, awolf@thch.uni-bonn.de

approximate the exact block-diagonal Dirac Hamiltonian H_{bd}

$$H_{bd} = \sum_{k=0}^n \mathcal{E}_k + \sum_{k=n+1}^{\infty} \mathcal{E}_k = H_{DKHn} + \mathcal{O}(\tilde{V}^n), \quad (4)$$

up to $(n-1)$ -th order in \tilde{V} . The reason for this peculiarity lies, of course, in the independence of the initial fpFW transformation U_0 of the damped potential \tilde{V} and the fact that the fpFW Hamiltonian H_1 does not contain an odd term of zeroth order. Application of the first $m+1$ unitary transformations $U_m \cdots U_1 U_0$ to the Dirac Hamiltonian H_D yields the intermediate Hamiltonian

$$H_{m+1} = \left[\prod_{k=m}^0 U_k \right] H_D \left[\prod_{k=0}^m U_k^\dagger \right] \\ = \sum_{k=0}^{2m+1} \mathcal{E}_k + \sum_{k=2m+2}^{\infty} \mathcal{E}_k^{(m+1)} + \sum_{k=m+1}^{\infty} \mathcal{O}_k^{(m+1)}, \quad (5)$$

that contains exactly $(2m+1)$ even terms which will not be altered by further unitary transformations [$(2m+1)$ -rule]. The even terms of higher order will be affected by subsequent unitary DKH transformations, which is indicated by a superscript in parenthesis attached to each term. Here and in the following we are employing exactly the same notation (symbols and abbreviations) as in part I of this series,¹ which might be consulted in order to avoid any ambiguities.

In recent years, the standard Douglas–Kroll–Hess procedure of second order,^{6,7} DKH2, has been extended to third,^{9,10} DKH3, fourth and fifth,^{8,11} DKH4 and DKH5, respectively, and very recently to sixth order,^{12,13} DKH6. Furthermore, also highly sophisticated implementations of the DKH method were published taking explicitly care of spin-dependent terms^{14–18} and the transformation of the two-electron interaction.^{15,19}

In this work, we present the first realization of an arbitrary and thus infinite-order DKH scheme, i.e., an analytic decoupling procedure for the Dirac Hamiltonian up to any given order in \tilde{V} . We start with the introduction of the basic notation in Sec. II, where it is also explained how exact decoupling can be achieved within the generalized DKH framework. The following Sec. III explicates how the maximum order necessary for this purpose can be deduced. The algorithmic details are described in Sec. IV and a discussion of the scaling behavior of this algorithm with respect to computational requirements may be found in Sec. V. Numerical results for one- and many-electron atoms are given in Sec. VI, and Sec. VII concludes this study.

II. INFINITE-ORDER DKH

In any computational scheme, “exact” decoupling is reached if the truncation error $\mathcal{O}(\tilde{V}^n)$ defined by Eq. (4) is of the order of the arithmetic precision of the computer, or at least negligible with respect to the physical or chemical issues under investigation. Given a molecular system and a desired numerical accuracy τ , we do consequently need an evaluation protocol for the *a priori* determination of the cutoff order n_{opt} of the DKH expansion, beyond which no fur-

ther numerical improvement (relevant for τ) will be achieved. Higher-order corrections $\mathcal{E}_{k>n_{\text{opt}}}$ will thus only yield insignificant fluctuations of total and relative energies and properties. For the numerical set up of the exact, block-diagonal Dirac Hamiltonian H_{bd} it is thus sufficient to restrict to the finite-order $DKHn_{\text{opt}}$ Hamiltonian, since the truncation error is guaranteed to be numerically negligible. In other words, numerical convergence of the DKH energies towards the exact Dirac energy is already achieved by restriction to the $DKHn_{\text{opt}}$ scheme, which thus represents the optimal DKH approximation optimizing the balance between accuracy and computational cost.

It is exactly this possibility of determining the required maximum order n_{opt} prior to a quantum chemical calculation, which makes the DKH protocol a feasible infinite-order decoupling method. Otherwise, if this truncation criterion, which will be deduced in detail in Sec. III, were not available, one would have to test each order in a complete electronic structure calculation to check convergence of the energy expectation values. Note that infinite-order decoupling in the purely numerical Barysz–Sadlej–Snijders (IOTC) method⁴ actually relies on exactly the same philosophy: iterative evaluation of the one-step unitary transformation employed in the IOTC protocol is stopped, as soon as a certain numerical precision has been reached.

Let us assume the intermediate Hamiltonian H_{m+1} after the first $m+1$ unitary transformation steps defined by Eq. (5) were given. Application of the next unitary transformation U_{m+1}

$$H_{m+2} = U_{m+1} H_{m+1} U_{m+1}^\dagger \quad (6)$$

$$= \sum_{k=0}^{2m+3} \mathcal{E}_k + \sum_{k=2m+4}^{\infty} \mathcal{E}_k^{(m+2)} \\ + \underbrace{\mathcal{O}_{m+1}^{(m+1)} + a_{m+1,0} a_{m+1,1} [W_{m+1}, \mathcal{E}_0]}_{\mathcal{O}_{m+1}^{(m+2)}} \\ + \sum_{k=m+2}^{\infty} \mathcal{O}_k^{(m+2)} \quad (7)$$

$$= H_{DKH(2m+3)} + \mathcal{O}(\tilde{V}^{2m+3}), \quad (8)$$

yields all terms contributing to the DKH Hamiltonians up to order $2m+3$, where for the sake of simplicity the irrelevant odd terms with orders between $m+2$ and $2m+3$ in the external potential V have been omitted in Eq. (8). The unitary transformation U_{m+1} —as all unitary matrices employed before—is constructed as the most general power series ansatz in terms of the anti-Hermitian odd operator W_{m+1}

$$U_{m+1} = a_{m+1,0} \mathbf{1} + \sum_{j=1}^{\infty} a_{m+1,j} W_{m+1}^j. \quad (9)$$

Equation (9) defines the *generalized* Douglas–Kroll–Hess method,^{8,11} because the most general analytic expressions for the DKH Hamiltonians are obtained, covering all different unitary parametrizations used in the literature. Note that the term W_{m+1}^j is of exactly $[j \cdot (m+1)]$ -th order in \tilde{V} . Therefore, for a consistent derivation of all relevant terms of the

DKH $_{\text{opt}}$ Hamiltonian, we have to take all terms contributing to the unitary transformations U_i with orders $i \cdot k$ into account, with $k=0,1,\dots,\text{int}(n_{\text{opt}}/i)$ according to the $(2n+1)$ -rule. Consequently, the inner unitary transformations, which are parametrized by W_i -operators of lower order in the external potential have to be expanded up to higher powers according to Eq. (9) than the outer unitary transformations.

W_{m+1} is determined uniquely by the requirement that it has to account for the elimination of the odd term $\mathcal{O}_{m+1}^{(m+2)}$. Being an integral operator of $(m+1)$ -th order, this is guaranteed if and only if the kernel of W_{m+1} is given by

$$W_{m+1}(p_0, p_1, \dots, p_{m+1}) = \frac{a_{m+1,0}}{a_{m+1,1}} \beta \frac{\mathcal{O}_{m+1}^{(m+1)}(p_0, p_1, \dots, p_{m+1})}{E_{p_0} + E_{p_{m+1}}}. \quad (10)$$

If the matrix representation of this kernel were known, one could immediately employ it to evaluate all terms of the DKH Hamiltonian $H_{\text{DKH}(2m+3)}$. This procedure could be repeated until the resulting Hamiltonian is block-diagonal up to any desired order in V (determined by machine precision).

It is, however, exactly this step which is not feasible within any two-component implementation, since the matrix representations of odd operators must not be calculated. As mentioned above and discussed in detail in part I,¹ their evaluation would inevitably require the introduction of basis sets for the small components of the molecular spinors, which are approximately twice as large as the large component basis sets and have to contain exponents for higher angular momentum functions due to the requirements of kinetic balance. This would not only blow up the computational costs of the calculations considerably, but even destroy the elegant framework of one- or two-component relativistic methods, which could no longer be easily embedded into every nonrelativistic computer code. As a matter of fact, exactly the same integrals would appear as in fully relativistic four-component codes, and no savings were obtained by the block-diagonalization of the Hamiltonian. We thus have to restrict to a symbolic closed-form evaluation of the even terms \mathcal{E}_k employing a suitable DKH parser algorithm which is presented in Sec. IV.

III. PRE-DETERMINATION OF THE MAXIMUM DKH ORDER REQUIRED

The necessary order n_{opt} for exact decoupling—depending on the system under investigation—can be determined prior to any quantum chemical calculation due to the exact knowledge of the expansion parameter [cf., part I]: Each term contributing to the even term \mathcal{E}_k of the DKH Hamiltonian of Eq. (3) features exactly $k-1$ huge energy denominators due to the damped external potential

$$\tilde{V}_{ij} = \frac{V_{ij}}{E_i + E_j}, \quad (11)$$

with $E_{p_i} = \sqrt{p_i^2 c^2 + m^2 c^4}$ being the relativistic energy–momentum relation. In order to keep the notation as simple as possible, we will continue to denote \mathcal{E}_k as being of $(k-1)$ -th order in \tilde{V} , though obviously it cannot always be

decomposed into $k-1$ separate factors of \tilde{V} , but might also contain terms with nested energy denominators like W_2 (cf. Ref. 1). Due to the structure of the fpFW Hamiltonian

$$H_1 = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1 \quad (12)$$

$$= \beta E_p - mc^2 + A_p (V + R_p V R_p) A_p + \beta A_p [R_p, V] A_p, \quad (13)$$

with

$$A_p = \sqrt{\frac{E_p + mc^2}{2E_p}}, \quad (14)$$

$$R_p = \mathcal{R}_p \boldsymbol{\alpha} \cdot \mathbf{p} = \frac{c \boldsymbol{\alpha} \cdot \mathbf{p}}{E_p + mc^2}, \quad (15)$$

each even term \mathcal{E}_k comprises at least a factor of $A_p \mathcal{R}_p V \mathcal{R}_p A_p \cdot (A_p \tilde{V} A_p)^{k-1}$. Within a semiclassical analysis this factor assumes its maximum value for vanishing momentum p , and is thus always guaranteed to have a smaller operator norm than the truncation estimate operator

$$\mathcal{V}_k = (4m^2 c^2)^{-1} \cdot A_p V A_p \cdot (A_p \tilde{V} A_p)^{k-1}. \quad (16)$$

The order of magnitude of the term \mathcal{E}_k can thus be estimated by investigating the eigenvalues $\alpha_i^{(k)}$ of this truncation estimate operator \mathcal{V}_k , which will of course depend on the system under investigation, i.e., the largest nuclear charge Z of the nuclei occurring in the molecule and the basis set chosen. As soon as the absolute value of the largest eigenvalue of \mathcal{V}_k is below the chosen truncation threshold τ , $|\alpha_{\text{max}}^{(k)}| < \tau$, the higher-order even terms \mathcal{E}_l with $l > k$ will only affect the total energy of the system under investigation beyond the desired accuracy established by τ .

In Table I the largest absolute value of the eigenvalues $\alpha_i^{(k)}$ of \mathcal{V}_k for one-electron atoms with nuclear charges $Z = 20, 40, 60, 80$, and 100 is presented. For all truncation analyses we have employed the same large even-tempered Gaussian basis set as for the energy calculations in Sec. VI A (see below). According to our truncation criterion, DKH8, DKH11, DKH14, DKH16, and DKH18, respectively, should be sufficient for the five ions presented in Table I if an overall absolute accuracy for total energies of $\tau = 10^{-5}$ is sought for. These optimal DKH orders n_{opt} have to be increased to 10, 14, 17, 20, and 23, respectively, if the tighter truncation threshold of $\tau = 10^{-8}$ is chosen.

A comparison of these *a priori* determined optimal orders n_{opt} to the actually calculated DKH energies for these systems (cf. Table V) reveals that our truncation criterion is very tight. The DKH energies appear to converge even faster towards the desired accuracy limit given by τ than it has been estimated. For example, for a nuclear charge of $Z = 20$ (Ca) already DKH5 and DKH8 yield total energies with 5 and 8 decimal figures which are not affected by higher-order corrections, respectively. And for $Z = 60$ (Nd) DKH13 is already capable of guaranteeing five correct decimals places.

Consequently, the truncation criterion based on the analysis of the eigenvalues of the truncation estimate operator \mathcal{V}_k has thus to be understood as an approximate, yet very reliable estimate for the determination of the necessary DKH order for exact decoupling of the Dirac Hamiltonian. Decou-

TABLE I. Largest absolute value $|\alpha_{\max}^{(k)}|$ of the eigenvalues $\alpha_i^{(k)}$ of the truncation estimate operator \mathcal{V}_k for different nuclear charges Z . $\text{sgn}(\alpha^{(k)})$ denotes the sign of the eigenvalues of \mathcal{V}_k . The even-tempered Gaussian basis set described in Sec. VI A has been employed. The corresponding optimal DKH orders n_{opt} for exact decoupling due to the truncation error analysis for two different truncation thresholds τ are given in the last two lines of the Table.

k	$\text{sgn}(\alpha^{(k)})$	$Z=20$	$Z=40$	$Z=60$	$Z=80$	$Z=100$
1	—	2.394 38E+5	4.648 39E+6	1.992 27E+7	2.805 78E+7	2.995 38E+7
2	+	3.198 40E+3	2.135 68E+5	1.399 14E+6	2.654 61E+6	1.685 06E+6
3	—	1.170 40E+2	1.452 68E+4	1.446 25E+5	3.690 92E+5	2.059 76E+5
4	+	4.933 07E+0	1.111 58E+3	1.673 29E+4	5.743 07E+4	3.865 63E+4
5	—	2.177 87E−1	8.877 97E+1	2.014 56E+3	9.297 84E+3	8.041 19E+3
6	+	9.861 77E−3	7.243 94E+0	2.472 19E+2	1.534 21E+3	1.731 11E+3
7	—	4.543 06E−4	5.992 85E−1	3.069 01E+1	2.560 95E+2	3.803 28E+2
8	+	2.120 23E−5	5.012 26E−2	3.841 27E+0	4.310 17E+1	8.470 33E+1
9	—	9.999 59E−7	4.235 01E−3	4.839 24E−1	7.301 96E+0	1.904 77E+1
10	+	4.758 48E−8	3.617 33E−4	6.130 54E−2	1.244 06E+0	4.314 10E+0
11	—	2.282 51E−9	3.129 28E−5	7.805 47E−3	2.130 40E−1	9.824 20E−1
12	+		2.749 76E−6	9.984 39E−4	3.665 69E−2	2.246 66E−1
13	—		2.462 37E−7	1.282 80E−4	6.336 18E−3	5.155 06E−2
14	+		2.251 64E−8	1.655 10E−5	1.100 04E−3	1.186 06E−2
15	—		2.101 13E−9	2.144 14E−6	1.917 97E−4	2.734 92E−3
16	+			2.788 57E−7	3.358 05E−5	6.318 25E−4
17	—			3.640 47E−8	5.903 50E−6	1.461 98E−4
18	+			4.770 08E−9	1.042 03E−6	3.387 60E−5
19	—				1.846 59E−7	7.859 19E−6
20	+				3.285 22E−8	1.825 35E−6
21	—				5.867 38E−9	4.243 83E−7
22	+					9.876 02E−8
23	—					2.300 35E−8
24	+					5.362 64E−9
$n_{\text{opt}}(\tau=10^{-5})$		8	11	14	16	18
$n_{\text{opt}}(\tau=10^{-8})$		10	14	17	20	23

pling up to the chosen threshold τ might in practice be obtained even earlier, i.e., for lower-order DKH Hamiltonians. But the $\text{DKH}n_{\text{opt}}$ Hamiltonians suggested by this truncation analysis will not fail to yield the desired accuracy, which is confirmed by the numerical results presented in Sec. VI.

The well-known alternating pattern of the DKH energies⁸ can already be anticipated by inspection of the sign $\text{sgn}(\alpha^{(k)})$ of the eigenvalues of \mathcal{V}_k . Odd orders ($k=1,3,5,\dots$) do always feature negative contributions to the DKH energy whereas even-order terms ($k=2,4,\dots$) do always increase the energy as compared to the previous order. We note that all eigenvalues $\alpha_i^{(k)}$ of the truncation estimate operator \mathcal{V}_k feature the same sign, i.e., they are either all positive (k even) or all negative (k odd).

Finally, we emphasize that within any basis set approach exact decoupling does, of course, only guarantee convergence towards the basis set limit and not towards the exact analytic Dirac limit. For any practical calculation the truncation threshold τ should thus consequently be chosen in accordance with the deficiency inherent in the basis set: The larger and better the basis set, the smaller the threshold τ might be sensibly chosen, since it would not make any sense to decouple up to an accuracy of $\tau=10^{-8}$, for example, if the basis set employed is only capable of guaranteeing milli-Hartree accuracy. For most quantum chemical calculations employing standard basis sets of, e.g., triple zeta quality, decoupling up to $\tau=10^{-4}$ appears thus to be sufficient.

IV. GENERATION OF DKH OPERATORS OF ARBITRARY ORDER

As discussed above, the evaluation of the DKH Hamiltonian up to any predefined order in the external potential requires a new computational scheme, which cannot rely on a purely numerical iterative method. Therefore, each order of the decoupled DKH Hamiltonian has to be determined purely algebraically, i.e., by *symbolical* evaluation of the corresponding unitary transformations. Due to the increasing complexity of the higher-order terms, their determination, however, is only possible if the algebraic operations are evaluated automatically by a suitable parser routine yielding analytic formulas for each order \mathcal{E}_k . Subsequently, this parser should be able to translate the resulting closed-form operator expressions into corresponding matrix multiplications arising in any basis set expansion. The basic layout and the efficient implementation of such a parser routine will be described in this section.

A. Starting point for the symbolic procedure

The starting point for the symbolic operations to be performed by the parser routine is the free-particle Foldy–Wouthuysen Hamiltonian H_1

$$H_1 = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{O}_1, \quad (17)$$

TABLE II. Overview of all high-level expressions employed within the symbolic parser procedure. The high-level expressions are described in detail in Sec. IV C.

Quantity	Definition	High-level code
\mathcal{E}_0	$\beta E_p - mc^2$	E00
\mathcal{E}_1	$A_p(V + R_p V R_p) A_p$	E01
\mathcal{O}_1	$\beta A_p[R_p, V] A_p$	O01
W_i	cf. Eq. (10)	Wxx
S_i	cf. sect. IV C	Sxxx
T_i	$R_p S_i R_p$	Txxx

which is represented here in its “high-level” form. This operator is formally stored as a vector with three components according to

$$H_1 \rightarrow \begin{pmatrix} (0, +1, +1.0, \mathcal{E}_0) \\ (1, +1, +1.0, \mathcal{E}_1) \\ (1, -1, +1.0, \mathcal{O}_1) \end{pmatrix}. \quad (18)$$

Each entry of this high-level Hamiltonian vector in pseudo-code notation is characterized by the structure

(order, symm, coeff, string),

where the integer **order** specifies the order in the external potential V and **symm** describes the even (+1) or odd (−1) structure of this term. The real variable **coeff** is the prefactor of the corresponding term and the character string **string** labels the actual form of this term. We have chosen the phrase “high-level” expression here in order to emphasize that the specific form of each term contributing to H_1 is *not* resolved into computable expressions at this stage. In general, high-level expressions do only contain the quantities \mathcal{E}_0 , \mathcal{E}_1 , \mathcal{O}_1 , the W -operators W_i , and combinations of these quantities for which new shortcuts might be introduced in the second step, cf. Sec. IV C. For instance, we have thus not replaced the high-level term \mathcal{O}_1 by its low-level constituents, i.e.,

$$(1, -1, +1.0, \mathcal{O}_1) \rightarrow \begin{pmatrix} (1, -1, +1.0, \beta A_p R_p V A_p) \\ (1, -1, -1.0, \beta A_p V R_p A_p) \end{pmatrix}, \quad (19)$$

which would show a closer resemblance to the actual matrix operations to be performed by any DKH program. However, this would lead to a fpFW Hamiltonian with five components instead of three, which would in turn dramatically increase the computational complexity in subsequent steps. Hence, the huge computational complexity, which is due to the large number of components comprised by these high-level expressions is postponed to a later step of the algorithm. The advantage of this procedure is that symbolic manipulations on the resulting high-level Hamiltonians are much less computer time demanding.

In Table II a summary of all high-level expressions employed by the algorithm is presented. The numerical evaluation in terms of matrix multiplications requires, of course, low-level expressions which are entirely reduced to the most fundamental quantities.

In order to understand the symbolic operations performed by this algorithm it is essential to realize that all operators containing the momentum operator—like A_p and

R_p —do commute with each other, but they all do not commute with any operator containing the external potential V .

B. Step 1: Symbolic construction of the high-level DKH Hamiltonian

As soon as the desired order $n_{\text{opt}} \equiv n$ up to which decoupling shall be achieved has been fixed, the high-level expressions of all necessary unitary transformations U_i [$i = 1, 2, \dots, \text{int}(n/2)$] can be constructed. From now on we will consequently use n instead of n_{opt} to denote the desired order of decoupling for the sake of brevity. For any real number α , $\text{int}(\alpha)$ denotes the largest integer lower or equal to α , and due to the $(2n+1)$ -rule no further unitary transformations are required. For algorithmic reasons all these $\text{int}(n/2)$ transformations cannot be simultaneously constructed at the very beginning, but they have to be consecutively processed. The following subsections (Secs. IV B 1–IV B 4) are thus to be executed for each transformation U_i of the sequence of unitary transformations.

1. Construction of the unitary transformation U_i

The high-level expressions of unitary transformations U_i are represented by vectors with $\text{int}(n/i) + 1$ components, whose $(k+1)$ -th entry is given by

$$(ki, (-1)^k, a_{i,k}, W_i^k)$$

$$\triangleq (ki, (-1)^k, a_{i,k}, W_{xx} W_{xx} \dots W_{xx}).$$

The first entry ($k=0$) is simply the unity operator and the coefficients $a_{i,k}$, of course, have to satisfy the unitarity conditions. According to Table II each operator W_i is stored as a 3-character string W_{xx} , i.e., W_1 is coded as $W01$. This setup is thus flexible enough to allow for the construction of the first 99 unitary transformations. The Hermitian conjugate transformation U_i^\dagger is constructed by changing the sign of the odd coefficients $a_{i,2k+1}$. In order to obtain an overall consistent order of n , inner unitary transformations (low value of i) have to be expanded up to higher powers of W_i than outer transformations. For instance, the first unitary transformation U_1 contains $n+1$ components, whereas the last transformation [$i = \text{int}(n/2)$] contains only three components, since it has to be expanded up to $W_{\text{int}(n/2)}^2$. We note in passing that the last component of W_i can always be neglected if it is an odd term of exactly n th order.

Before the transformation U_i may be applied to the intermediate Hamiltonian H_i , we have to store the high-level form of the odd operator W_i in order to reduce the final Hamiltonian to its low-level representation in step 3, cf. Sec. IV D. According to Eq. (10) W_i contains all odd terms of H_i which are of i th order, furnished with β and an energy denominator. In order to make handling of the resulting expressions feasible, these energy denominators are symbolized by surrounding brackets, i.e., the first W -operator W_1 is stored as

$$W_1 \rightarrow (1, -1, +1.0, \beta[\mathcal{O}_1]) \triangleq (1, -1, +1.0, \beta[\text{O01}]), \quad (20)$$

and contains only one high-level component, whereas W_2 is represented by

$$W_2 \rightarrow \begin{pmatrix} (2, -1, +1.0, \beta[W_1 \mathcal{E}_1]) \\ (2, -1, -1.0, \beta[\mathcal{E}_1 W_1]) \end{pmatrix} \\ \triangleq \begin{pmatrix} (2, -1, +1.0, \beta[W01E01]) \\ (2, -1, -1.0, \beta[E01W01]) \end{pmatrix}. \quad (21)$$

The number of high-level components of higher W -operators grows significantly and depends slightly on the chosen parametrization of the unitary transformations. A detailed discussion of this scaling behavior is postponed to Sec. V.

2. Execution of the unitary transformation U_i

As soon as U_i and U_i^\dagger are set up, they are applied to the intermediate Hamiltonian H_i , which yields the new Hamiltonian

$$H_{i+1} = U_i H_i U_i^\dagger = H_{i+1}(\mathcal{E}_0, \mathcal{E}_1, \mathcal{O}_1, W_1, \dots, W_i). \quad (22)$$

At this stage the high-level Hamiltonian H_{i+1} contains only a few ingredients, namely the three fpFW components and the first i W -operators. Since each of the three “vectors” to be multiplied bears terms up to n th order, most terms arising out of these two multiplications feature an order higher than n and are thus immediately disregarded. Finally, all resulting terms of H_{i+1} are sorted in ascending order in the external potential in order to reduce the computational demands for the next iteration with U_{i+1} , since the order of products can thus easily be determined in advance.

3. Exploitation of commutator symmetry

Further simplification of the resulting Hamiltonian H_{i+1} is achieved by exploitation of the commutator relation

$$[W_i, \mathcal{E}_0] = -\mathcal{O}_i^{(i)}, \quad (23)$$

which is nothing else but the fundamental equation defining W_i , cf. Eqs. (10) and (7). Note that we have set $a_{i,0} = a_{i,1} = 1$ here, which can always be assumed without loss of generality.⁸ Due to this relation all occurrences of \mathcal{E}_0 within the Hamiltonian H_{i+1} are eliminated (except of the zeroth-order term \mathcal{E}_0 , of course, which is not affected by the whole symbolic procedure at all). Hence, the Hamiltonians H_{i+1} can be characterized by

$$H_{i+1} = H_{i+1}(\mathcal{E}_1, \mathcal{O}_1, W_1, \dots, W_i). \quad (24)$$

4. Elimination of all noncontributing terms

Finally, all terms which will not affect the desired final DKH Hamiltonian are removed from the Hamiltonian H_{i+1} . First of all, all lowest-order odd terms $\mathcal{O}_i^{(i+1)}$, i.e., the odd terms of order i are removed, since they perfectly cancel due to the conditional equation for W_i , cf. Eq. (7). Furthermore, all odd terms with orders higher or equal to $n-i$ are removed, since they cannot in principle contribute to even terms with order lower or equal to n in subsequent transformation steps. If the last transformation U_i has been performed, i.e., $i = \text{int}(n/2)$, all odd terms occurring in the final Hamiltonian can, of course, be neglected. All terms, which occur more than once in the Hamiltonian are subsequently summarized, and all terms with coefficients $\text{coeff}(a_{i,k})$ below a certain zero threshold (adjusted to machine precision)

TABLE III. Number of high-level components of each even operator \mathcal{E}_k for different choices of the parametrization of the unitary transformations U_i . $H_{\text{DKH}20}$ comprises all terms up to 20th order. A zero threshold of 10^{-14} has been employed for all calculations. Note that a less tight but still reliable zero threshold would reduce the number of components contributing to each term. See text for further details.

	U^{SQ}	U^{McW}	U^{opt}	U^{exp}	U^{CA}
\mathcal{E}_0	1	1	1	1	1
\mathcal{E}_1	1	1	1	1	1
\mathcal{E}_2	2	2	2	2	2
\mathcal{E}_3	3	3	3	3	3
\mathcal{E}_4	8	8	8	8	8
\mathcal{E}_5	12	10	14	14	14
\mathcal{E}_6	24	26	28	30	30
\mathcal{E}_7	38	39	45	45	45
\mathcal{E}_8	76	82	84	88	88
\mathcal{E}_9	107	107	137	137	137
\mathcal{E}_{10}	186	212	236	246	246
\mathcal{E}_{11}	271	309	363	371	371
\mathcal{E}_{12}	464	546	592	626	626
\mathcal{E}_{13}	667	769	907	939	939
\mathcal{E}_{14}	1058	1286	1430	1506	1506
\mathcal{E}_{15}	1492	1843	2111	2199	2199
\mathcal{E}_{16}	2308	2928	3230	3410	3410
\mathcal{E}_{17}	3216	4100	4724	4932	4932
\mathcal{E}_{18}	4770	6298	7024	7416	7418
\mathcal{E}_{19}	6616	8878	10 062	10 554	10 558
\mathcal{E}_{20}	9666	13 210	14 670	15 490	15 502
$H_{\text{DKH}20}$	30 986	40 658	45 672	48 018	48 036

are neglected. As a consequence, cancellation of identical terms with opposite sign is not accomplished exactly but only up to a tiny residual component, e.g., up to 10^{-20} . For all calculations presented in this study we have employed the very rigid zero threshold of 10^{-14} , which must not be confused with the truncation threshold τ introduced in Sec. III. In general, these two thresholds have nothing in common, and they have to be fixed independently of each other. Our zero threshold of 10^{-14} might be relaxed significantly in order to allow efficient prescreening of terms to reduce the computational effort, which is discussed in Sec. V, where the computational scaling behavior of the DKH Hamiltonians is analyzed.

After Secs. IV B 1–IV B 4 have been executed for all unitary transformations U_i , the high-level expressions of all even terms \mathcal{E}_k contributing to the final Hamiltonian $H_{\text{DKH}n}$ given by Eq. (3) are available, i.e., the analytic expression for the DKH n Hamiltonian has been derived. Depending on the zero threshold and the parametrization of U_i , the number of components of \mathcal{E}_k varies. This scaling of the number of terms contributing to each order \mathcal{E}_k is presented in Table III for five different parametrizations up to order 20 and is discussed in Sec. V.

C. Step 2: High-level substitution procedure

After the high-level form of the DKH Hamiltonian has been set up, one could immediately start to reduce it directly to its low-level form. Such a procedure would, however, be extremely unfavorable, since a large number of operator products does occur many times and should not be recomputed again and again if an efficient implementation is

sought for. For instance, even for the DKH10 Hamiltonian the product W_1^2 does occur 538 times, and should thus only be evaluated once.

Consequently, products of the form $W_i W_j$ and $W_i \mathcal{E}_1 W_j$, which are represented by 6- and 9-character expressions in the code, respectively, are substituted by suitable S_i operators, which are represented by Sxxx patterns according to Table II. Up to 14th order a maximum number of 98 S_i expressions is sufficient.

Substitution by these S_i operators is executed for both the Hamiltonian and the W -operators in order to achieve the largest simplification possible. Due to the odd structure of the W -operators, they do, however, always contain an odd number of odd operators; i.e., after the S_i substitution process for the W -operators, there will always be at least one odd operator left to be processed later. For example, the first entry of W_3 will be substituted according to

$$(3, -1, +0.33, B[W01W01O01]) \rightarrow (3, -1, +0.33, B[S003O01]). \quad (25)$$

These resulting odd operators (like here $\mathcal{O}_1 \triangleq O01$) will subsequently give rise to new even structures $T_i = R_p S_i R_p$ coded as Txxx, which do thus also have to be stored for later steps. As a consequence, after this high-level substitution process the DKH Hamiltonian can be characterized by

$$H_{\text{DKH}n} = H_{\text{DKH}n}(\mathcal{E}_1, S_i, W_1, \dots, W_{\text{int}(n/2)}), \quad (26)$$

where the number of contributing W -operators does now depend on the number of S_i -operators introduced: the more S_i -operators have been introduced, the less W -operators are still present in $H_{\text{DKH}n}$. The substitution process of step 2 completes the high-level manipulations of our symbolic algorithm.

D. Step 3: Reduction to low-level form

Now all high-level expressions for the Hamiltonian $H_{\text{DKH}n}$, and the S_i and T_i operators have to be reduced to a computable low-level form. First, all high-level W_i -operators are recursively replaced by their low-level constituents, which have been stored in step 1a (see Sec. IV B 1). This will frequently introduce the odd operator \mathcal{O}_1 , which has subsequently to be resolved by its final low-level expression

$$\mathcal{O}_1 \rightarrow \begin{pmatrix} (1, -1, +1.d0, \text{BPV}) \\ (1, -1, -1.d0, \text{BVP}) \end{pmatrix}. \quad (27)$$

Here B represents the Dirac β -matrix and P symbolizes the operator $\mathcal{R}_p = \alpha \cdot P_p$. Note that for a scalar-relativistic implementation of the DKH procedure, no 1-character expression for Dirac α -matrices has to be introduced, since all α -matrices cancel due to Dirac's relation for spin matrices (cf. part I). Furthermore, the external potential V and its damped variant \tilde{V} do always appear in combination with two diagonal A_p -factors. It is thus sufficient for the low-level stage of our algorithm to represent the product $A_p V A_p$ by the 1-character symbol V .

Note that during the reduction of the Hamiltonian to low-level form the S_i -operators must, of course, not be resolved; otherwise we would not gain any computational sav-

ings by their previous introduction. The low-level reduction of the S_i and T_i operators has thus to be performed after the reduction of the Hamiltonian, and higher S_i operators might still depend on lower S_j -operators ($j < i$) and on all T_i -operators in order to achieve the greatest computational savings possible.

After this brute-force reduction to low-level form the 1-character low-level symbolic expressions have to be suitably reordered. First, every β -matrix B will be moved to the very left of each term, taking into account that it anticommutes with P . Afterwards, the DKH resolution of the identity,

$$P_p \frac{1}{P_p^2} P_p \rightarrow P Q P = 1, \quad (28)$$

with $Q \triangleq 1/P_p^2$ is introduced in order to guarantee that the resulting expressions are strictly functions of p^2 or $p V p$ instead of the linear momentum operator p alone. It is one of the most essential features of the Dirac Hamiltonian and its block-diagonal representation that this is always possible for even operators, as it has been discussed in part I.¹ Finally, the positions of the brackets '[' and ']' representing energy denominators are reordered, such that the resulting symbolic expressions have a direct matrix counterpart in step 4. These final steps of reordering terms and exploiting the DKH resolution of the identity have to be performed separately for the Hamiltonian and for the S_i and T_i expressions.

The final step during this reduction to low-level form in step 3 is the introduction of suitable auxiliary matrices U_{xx} which represent products of 1-character low-level expressions. Since there will be at most 36 different U_{xx} expressions occurring in the final DKH Hamiltonian (irrespective of the chosen order), this final substitution process will dramatically reduce the number of matrix multiplications to be performed in the next step, cf. Sec. V.

E. Step 4: Transcription of the symbolic expressions into a matrix code

As soon as the DKH Hamiltonian $H_{\text{DKH}n}$ and the auxiliary operators S_i and T_i are completely reduced to their low-level form, they might be evaluated by sequences of matrix multiplications. Since the Hamiltonian depends on both S_i and T_i expressions and S_i depends on the T_i operators, one has to evaluate the T_i patterns first. Subsequently, the S_i expressions might be processed and finally the Hamiltonian can be evaluated order by order.

The basic principle of this transcription into matrix multiplications is exactly the same as for conventional low-order implementations of the DKH procedure⁶ and is thus not reprinted in this study. Details (diagonalization of the nonrelativistic kinetic energy, transformation to p^2 -space, etc.) might be found in Ref. 8.

After the evaluation of the DKH Hamiltonian up to the desired order, the DKH modified one-electron integrals might directly be passed over to the SCF or correlation routines.

V. ANALYSIS OF THE SCALING BEHAVIOR OF THE ARBITRARY-ORDER DKH ALGORITHM

In the last section the basic layout of a fully automatic symbolic algorithm for the construction and evaluation of the DKH Hamiltonians up to any predefined order has been presented. Being very favorable with respect to computational demandings for low orders, the DKH scheme becomes more elaborate for higher orders. In this section the scaling behavior of the DKH Hamiltonians $H_{\text{DKH}n}$ will thus be analyzed in detail.

Depending on the chosen parametrization of the unitary transformations U_i , the number of high-level terms contributing to the Hamiltonian and thus the number of matrix multiplications necessary for its evaluation varies. Our analysis will be focused on parametrizations which can be given in closed form, i.e., the traditional square-root parametrization $U^{\text{SQ}} = \sqrt{1+W^2} + W$,²⁰ the McWeeny choice $U^{\text{McW}} = (1+W) \cdot (1-W^2)^{-1/2}$,²¹ the exponential parametrization $U^{\text{exp}} = \exp(W)$, and the Cayley-type expression $U^{\text{CA}} = (2+W)/(2-W)$. Furthermore, also the optimal unitary parametrization U^{opt} from Ref. 8 is presented which minimizes the deviation from unitarity for truncated series expansions of Eq. (9). We note in passing that this choice for the parametrization of the unitary transformations is the best possible from a fundamental, i.e., theoretical point of view. It has been established without reference to any special atomic or molecular system, but only due to the mathematical properties of truncated series expansions of unitary transformations.⁸ It does, however, not guarantee that numerical results obtained with this parametrization are closer to the exact analytical results for each order and/or for any particular system.

Due to vanishing odd coefficients $a_{i,2k+1}$ ($k \geq 1$) the square-root parametrization originally proposed by Douglas and Kroll²⁰ features the smallest number of terms contributing to W_i . The symmetry properties of the expansion coefficients a_k for the McWeeny parametrization U^{McW} ($a_{2k} = a_{2k+1}$ for $k \geq 1$) and for the optimum parametrization U^{opt} ($a_{2k-1} = a_{2k}$ for $k \geq 3$) are the reason for the slightly more favorable scaling of these two parametrizations as compared to U^{exp} and U^{CA} , whose coefficients do not exhibit any symmetry.⁸ All other parametrizations feature the same scaling of the number of terms of W_i like the exponential parametrization.

This increase of the number of high-level terms contributing to higher-order W -operators is reflected by the increasing number of high-level terms comprised by the higher-order even terms \mathcal{E}_k of the DKH Hamiltonian. In Table III the number of these terms contributing to each order \mathcal{E}_k is given for the five different unitary parametrizations mentioned above. The square-root parametrization features significantly less terms than all other parametrizations, and due to the coefficient symmetries U^{McW} and U^{opt} are computationally less demanding than U^{exp} and U^{CA} . Note that due to their factorial suppression the coefficients a_k of U^{exp} tend more rapidly to zero than for U^{CA} , and since we have chosen a zero threshold of 10^{-14} there are slightly less terms contributing to $\mathcal{E}_{k \geq 18}$ for U^{exp} than for U^{CA} .

As already mentioned in step 1d, cf. Sec. IV B 4, the

TABLE IV. Number of matrix multiplications necessary for the evaluation of the DKH Hamiltonians $H_{\text{DKH}n}$ up to DKH14 for two different parametrizations (SQ and exp) of the unitary transformations. The computational effort for the DKH schemes without the exploitation of auxiliary operators (brute-force implementation) is compared to our efficient implementation taking advantage of the Sxxx, Txxx, and Uxx auxiliary operators. A zero threshold of 10^{-14} has been employed for all calculations. Note that the multiplication with diagonal matrices like Q is counted as an ordinary matrix multiplication here though the implementation takes full advantage of the diagonal structure of these matrices.

n	U^{SQ}		U^{exp}	
	brute-force	with auxiliary operators	brute-force	with auxiliary operators
2	12	12	12	12
3	44	30	44	30
4	432	88	432	88
5	1940	191	2116	193
6	20 440	1162	22 296	1174
7	100 716	2860	112 124	3042
8	911 648	17 510	1 021 136	19 523
9	4 861 764	40 476	5 546 132	46 050
10		243 948		276 924
11		564 064		635 297
12		3 295 045		3 717 944
13		7 443 367		8 457 531
14		42 864 903		48 970 529

chosen zero threshold of 10^{-14} is very tight, and it might be relaxed without any loss of accuracy. Since higher-order terms contribute orders of magnitude less to the total energy than first- or second-order terms, this zero threshold can be chosen dynamically depending on the order of the term which is processed at a given stage of the algorithm. The higher the order in the external potential of a term is, the larger (i.e., weaker) the zero threshold might be chosen without loss of accuracy. This will allow efficient prescreening of terms and will reduce the computational requirements for very high orders significantly. However, such a prescreening has not been applied here, and a discussion of computational savings obtained by this dynamical prescreening scheme will be presented elsewhere.²²

Finally we mention that the number of high-level terms contributing to \mathcal{E}_k presented in Table III does not depend on the number of auxiliary operators (Sxxx, Txxx, and Uxx) introduced during the symbolic procedure. The introduction of these auxiliary quantities will, however, strongly influence the number of matrix multiplications needed for the final evaluation of the DKH Hamiltonians, as it is shown by Table IV, where this total number of matrix multiplications required for the evaluation of the DKH Hamiltonians without the introduction of auxiliary operators is compared to the more favorable approach employing Sxxx, Txxx, and Uxx operators. The analysis of the number of matrix multiplications in Table IV is presented for two different parametrizations of the unitary transformations (U^{SQ} and U^{exp}). Note, however, that the multiplication with diagonal matrices like Q is counted as an ordinary matrix multiplication here though the implementation takes full advantage of the diagonal structure of these matrices.

Since the even operator \mathcal{E}_1 is frequently used throughout

TABLE V. One-electron ground-state energies for the DKH scheme employing the exponential parametrization for the unitary transformations in Hartree atomic units. For all calculations an even-tempered universal Gaussian basis set with 75 exponents has been used. The speed of light was $c = 137.035\,989\,5$, and DEQ denotes the analytical Dirac energies.

Z	20	40	60	80	100	120
nr	−200.000 000 00	−800.000 000 00	−1800.000 000	−3200.000 00	−5000.0000	−7200.000
DKH1	−201.341 496 11	−823.894 226 33	−1934.202 797	−3686.447 46	−6472.3942	−12 134.151
DKH2	−201.072 539 60	−817.615 779 96	−1893.897 686	−3523.324 90	−5906.1919	−9594.100
DKH3	−201.076 661 81	−817.820 117 49	−1895.844 065	−3533.119 58	−5942.3695	−9712.934
DKH4	−201.076 509 74	−817.804 856 85	−1895.627 057	−3531.708 57	−5936.4739	−9698.531
DKH5	−201.076 524 82	−817.808 104 08	−1895.702 943	−3532.462 50	−5941.5411	−9731.138
DKH6	−201.076 523 20	−817.807 385 74	−1895.676 850	−3532.101 20	−5938.3144	−9703.671
DKH7	−201.076 523 36	−817.807 518 48	−1895.683 887	−3532.225 33	−5939.5876	−9714.236
DKH8	−201.076 523 34	−817.807 492 70	−1895.681 834	−3532.177 00	−5938.9700	−9708.236
DKH9	−201.076 523 34	−817.807 498 59	−1895.682 550	−3532.200 16	−5939.3620	−9713.637
DKH10	−201.076 523 34	−817.807 497 14	−1895.682 282	−3532.188 44	−5939.1072	−9709.207
DKH11	−201.076 523 34	−817.807 497 47	−1895.682 374	−3532.193 69	−5939.2439	−9711.709
DKH12	−201.076 523 34	−817.807 497 40	−1895.682 342	−3532.191 26	−5939.1649	−9709.993
DKH13	−201.076 523 34	−817.807 497 42	−1895.682 354	−3532.192 49	−5939.2167	−9711.483
DKH14	−201.076 523 34	−817.807 497 40	−1895.682 350	−3532.191 84	−5939.1821	−9710.251
DEQ	−201.076 523 36	−817.807 497 83	−1895.682 356	−3532.192 15	−5939.1954	−9710.784

the DKH parser procedure for the set up of higher-order terms, it is not decomposed into its most basic constituents. The treatment of this term does thus correspond to exactly one matrix multiplication each time it occurs in higher-order terms. As a consequence, the evaluation of the auxiliary operator $S_{21} = W_3 \mathcal{E}_1 W_2$, for example, requires only 198 matrix multiplications with our implementation instead of 4480 matrix multiplications which have been reported for an implementation of the sixth-order DKH6 Hamiltonian.¹²

Furthermore, also diagonal matrices like P_p^2 and $1/P_p^2$ resulting from the DKH resolution of the identity (cf. Sec. IV D) were treated as requiring one complete matrix multiplication for the analysis presented in Table IV, though their actual evaluation is coded in a more efficient way. Up to DKH4 the number of matrix multiplications is, of course, independent of the chosen parametrization, but for higher-order schemes the square-root parametrization is slightly more favorable with respect to computational demands than the exponential parametrization. However, these differences are of the order of magnitude of 10% of the total number of matrix multiplications required, and do thus hardly play any role for a significant speedup of the algorithm.

Table IV clearly demonstrates, however, that the introduction of auxiliary operators (S_{xxx} , T_{xxx} , and U_{xx}) is an essential and mandatory pre-requisite for the efficient evaluation of the DKH Hamiltonians with higher order. Already H_{DKH10} is not feasible at all if one relies on a brute-force implementation of the DKH scheme without taking advantage of the auxiliary operators. And even for the sixth-order Hamiltonian H_{DKH6} the brute-force implementation requires ~ 20 times as much effort than our efficient realization of the DKH parser algorithm. This ratio is dramatically increased up to about 50 for DKH9. With our approach even the very accurate DKH14 scheme becomes feasible, though its evaluation requires approximately 43 (U^{SQ}) and 49 (U^{exp}) million matrix multiplications, respectively. These numbers will, however, be significantly reduced if dynamical prescreening

of terms relying on flexible zero thresholds for each order is exploited, as it will be discussed elsewhere.²²

VI. RESULTS

A. One-electron atoms

We have implemented the parser algorithm described in the last sections as a general purpose code, which can easily be interfaced with any nonrelativistic electronic structure program. In order to investigate the convergence behavior of the DKH series, first test calculations have been performed for one-electron hydrogenlike atoms with different nuclear charges Z , where the DKH results can be compared to the analytically known exact Dirac energies.

All calculations have been performed with an even-tempered universal Gaussian basis set comprising exponents from 0.001 up to about 10^{13} with an even-tempered ratio of 1.65. This dense basis set contains thus 75 exponents. The value for the speed of light $c = 137.035\,989\,5$ was taken from Ref. 23, and all calculations have been carried out with 64-bit accuracy. All DKH calculations have been performed with DKH Hamiltonians relying on the exponential parametrization of the unitary matrices. The dependence of fifth- and higher-order results on the chosen parametrization of the unitary transformation is very small and will be discussed in detail elsewhere.²²

In Table V the ground state energies for six different nuclear charges $Z = 20$ up to $Z = 120$ are presented for the nonrelativistic case as well as for the DKH Hamiltonians up to 14th order. For the hydrogenlike ion with $Z = 20$ the DKH series is already completely converged for DKH8, i.e., already the DKH8 Hamiltonian represents the exactly decoupled infinite-order Hamiltonian H_{bd} with sufficient accuracy. The tiny deviation of 2×10^{-8} Hartree of our decoupled DKH results from the analytical Dirac energy confirms that our large basis set is indeed capable of resolving these very small oscillations. The results for $Z = 20$ show that DKH5 and DKH8 are sufficient if one aims at an accuracy for total

energies of 10^{-5} and 10^{-8} , respectively. The truncation criterion based on the truncation estimate operator \mathcal{V}_k presented in Sec. III is thus indeed a rather conservative measure for the prediction of the optimal order n_{opt} .

For the heavier nuclei with $Z=40$ and $Z=60$ DKH14 does still yield an overall accuracy of 10^{-7} and 10^{-5} , respectively. This has to be compared to lower-order approximations like DKH4 and DKH6, which are only capable of guaranteeing one decimal place for $Z=60$ (Nd^{59+}). If one is interested in highly accurate total energies, i.e., in completely decoupled two-component Hamiltonians one has thus necessarily to go beyond those low-order approximations. Furthermore it is interesting to note that DKH4, which is the last order being independent of the chosen parametrization, is almost as accurate as the next variational Douglas–Kroll–Hess scheme DKH6 for $Z=60$. Major improvement on the accuracy is only accomplished with DKH10, which does give milli- and sub-milli-Hartree accuracy.

Also for even heavier nuclei with $Z=80$ up to $Z=120$ the necessity of higher orders is evident by inspection of the results of Table V. For $Z=80$ (Hg^{79+}) DKH14 is at least capable of guaranteeing milli-Hartree accuracy, whereas, for example, DKH6 does again only yield one decimal place as compared to the exact Dirac eigenvalue. But for super-heavy nuclei even DKH14 appears not to be sufficient to yield exactly decoupled Hamiltonians. According to our truncation analysis based on \mathcal{V}_k one would have to go to 27th order in the DKH series in order to guarantee decoupled results up to eight digits. Although our automatic decoupling algorithm is in principle able to achieve decoupling up to this order, we refrain from carrying out these very extensive calculations.

It should be emphasized that total energies are only of little importance in quantum chemistry. Furthermore, a certain number of accurate digits is much harder to obtain for systems with large total energy than for systems with smaller total energies. For a more suitable and fair comparison of the necessary order for exact decoupling one may calculate scaled ground state energies $E_{\text{scaled}} = -E/Z^2$ for the systems discussed above in Table V. Then, up to $Z=60$ already DKH12 guarantees exact results, and even for $Z=80$ the deviation of the scaled energy E_{scaled} from the exact Dirac eigenvalue is smaller than 10^{-7} for DKH14. However, lower-order approximations like DKH8 for example seem not to be suited if one aims at highly accurate (almost) decoupled results.

For $Z=120$ there is one further subtlety, which has already been observed in earlier studies^{5,8,12} and which can now be explained in view of higher orders: For systems with Z larger than 104 the third-order result DKH3 yields energies which are atypically too large and do thus approximate the exact Dirac eigenvalue better than the formally superior schemes DKH5, DKH7, and DKH9. However, even for these highly charged nuclei the DKH series does not feature any convergence problems, such that this atypical behavior of DKH3 seems to be due to some favorable internal error cancellation of the DKH operators. The alternating pattern of the DKH series, i.e., even orders do always increase the energy as compared to the previous odd scheme is, however, not affected.

TABLE VI. Hartree-Fock all-electron ground state (2S) energies E of the gold atom. A universal Gaussian basis set of the form $32s29p20d15f$ (Ref. 24) and the speed of light $c=137.035\,989\,5$ have been used for all calculations. The four-component Dirac–Fock (DFC) results have been obtained with MOLDIR (Ref. 26).

	E
nr	−17 865.394 387
DKH1	−19 339.308 840
DKH2	−18 993.722 129
DKH3	−19 014.295 209
DKH4	−19 011.347 295
DKH5	−19 012.812 403
DKH6	−19 012.147 430
DKH7	−19 012.364 326
DKH8	−19 012.284 261
DKH9	−19 012.318 821
DKH10	−19 012.303 145
DKH11	−19 012.309 484
DKH12	−19 012.306 813
DKH13	−19 012.307 995
DKH14	−19 012.307 457
DFC	−19 039.585 625

The one-electron investigations presented in this subsection have proven that exact decoupling is in practice possible with DKH Hamiltonians. The necessary order n_{opt} strongly depends on the system under investigation, and for moderately charged systems (up to $Z=60$) already DKH14 achieves this goal.

B. Many-electron systems

Besides the one-electron calculations presented in the last subsection we have also performed all-electron calculations on the neutral gold atom in its 2S ground state. Its electronic configuration is characterized by $[\text{Xe}]5d^{10}6s^1$. Exactly the same universal Gaussian basis set provided by Malli *et al.*²⁴ has been employed as in an earlier study on the generalized DKH transformation up to DKH5.⁸ This basis set contains $32s$, $29p$, $20d$, and $15f$ exponents with an even-tempered ratio of 2.05. The smallest exponent is 0.02 and its largest s -exponent is given by $\sim 10^9$.

We have performed nonrelativistic (nr) as well as relativistic DKH calculations up to 14th order, and the results are given in Table VI. All these calculations have been performed with an atomic Hartree–Fock program based on the work by Roothaan and Bagus,²⁵ which has been modified in order to include our arbitrary-order DKH package. The four-component Dirac–Fock–Coulomb (DFC) result has been obtained with MOLDIR.²⁶

Similar to the one-electron calculations presented above, also the total DKH energies of the gold atom feature the same characteristic alternating convergence behavior: Odd DKH orders do always lower the energy, while even orders yield a positive contribution to the energy and do thus increase it as compared to the value corresponding to the previous DKH order. The standard second-order DKH approximation, DKH2, is not able to yield reliable total energies for the gold atom, but the DKH series exhibits a quite rapid convergence pattern. Already DKH14 gives a total energy with better than milli-Hartree accuracy. Since the deficiency

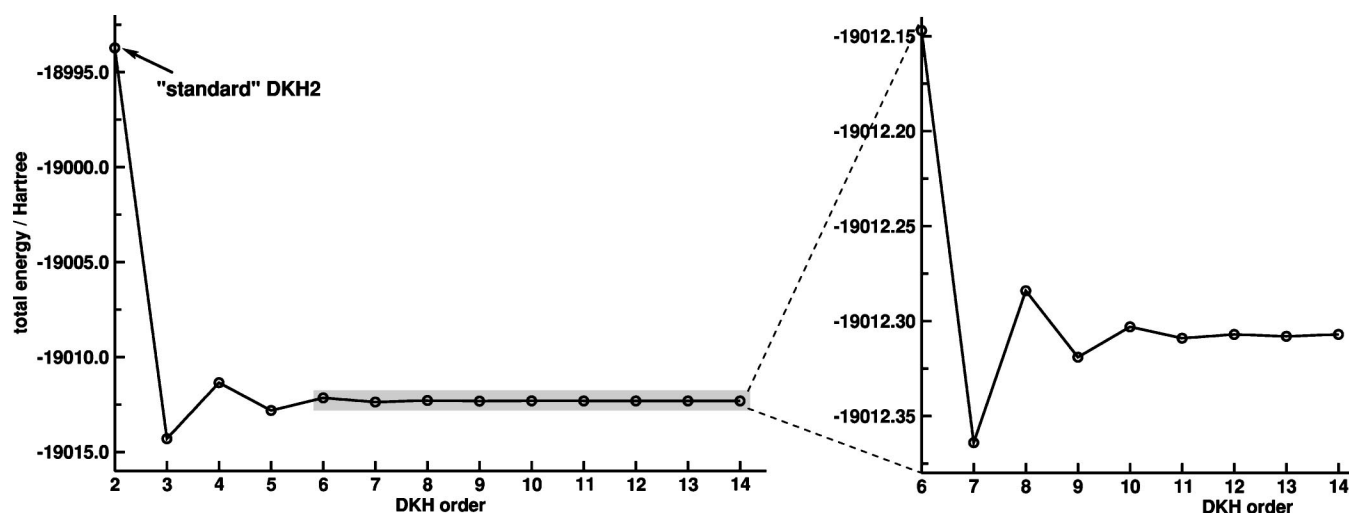


FIG. 1. Schematic representation of the ground state (2S) energy of the gold atom for different orders of the DKH scheme. Left: DKH n energies for $n=2$ up to $n=14$. Right: DKH n energies for $n \geq 6$, in order to resolve the convergence behavior of the DKH series.

of the basis set (≈ 0.005 Hartree for the nonrelativistic calculation) is of the same order of magnitude (or even larger), transition to higher DKH orders and further decoupling of the Hamiltonian would not make any sense. Consequently, in combination with this basis set DKH14 represents the final relativistic scheme for the gold atom.

As already discussed in extenso in Ref. 8 we should emphasize that the four-component DFC result, which is given in the last line of Table VI, must not be considered as the DKH limit, since we have applied the usual scalar-relativistic DKH variant for the one-electron terms only. The gap between the DFC result and this scalar-relativistic DKH limit is ~ 27 Hartree and is due to the neglect of the DKH transformation of the two-electron terms and the spin-dependent terms.⁸

The convergence behavior of the DKH series is illustrated graphically by Fig. 1. We have chosen two different scales for the (vertical) energy axis in order to resolve the tiny fluctuations of higher-order DKH corrections as compared to the comparatively large oscillations of the energy up to DKH8. The shaded rectangular block (DKH6–14) on the left hand side of Fig. 1 is magnified on the right side of Fig. 1, where the energy axis does only cover a region of 0.2 Hartree (as compared to 20 Hartree on the left hand side of the diagram). Otherwise the higher-order corrections could not be resolved at all, reflecting the fast convergence of the DKH series.

Finally, we emphasize that our flexible implementation of the DKH parser algorithm discussed in this study can immediately be transferred to molecular electronic structure calculations as its interface requires only T , V , and pVp integral matrices.

VII. CONCLUSION

In this second part of our series of papers on exact decoupling of the Dirac Hamiltonian we have successfully pursued to implement a general evaluation scheme for arbitrary-order Douglas–Kroll–Hess calculations. With this machi-

nery, we have obtained results up to 14th order for one- and many-electron systems for the first time, and have demonstrated that exact decoupling can be achieved in practice within the DKH scheme (as predicted from our rigorous formal analysis in part I). In order to shortly recall the achievements in this work, we may summarize the following points:

- An infinite-order DKH scheme requires a step-by-step *symbolic* evaluation of DKH Hamiltonians (as shown in part I). This automatic symbolic evaluation has been described and implemented into a general purpose program package, which can be easily interfaced with any nonrelativistic electronic structure program.
- A corner stone of the infinite-order DKH method is the *a priori* determination of the highest order necessary for decoupling up to machine precision. Here, we have utilized the formal analysis from part I to obtain a truncation error criterion, which allows us to determine the necessary decoupling order for a *de facto* infinite-order DKH calculation prior to its evaluation.
- The truncation criterion for the *a priori* determination of the DKH order was chosen to be very tight. The actual calculations show that it may be softened by some orders of magnitude to account for other method-inherent approximations like the size of the basis set.
- Special care has been taken for the reduction of the number of matrix multiplications, which increases dramatically from order to order. The efficiency of our algorithm becomes evident at, for instance, tenth order, where the evaluation of the DKH10 Hamiltonian took only a couple of minutes on a modern personal computer. Although the standard second-order DKH2 method will be sufficient in most cases of chemical interest (see Ref. 27), DKH Hamiltonians with orders even as high as DKH10 or DKH12 do not require much more additional effort.
- We obtained energy eigenvalues from exactly decoupled DKH Hamiltonians for highly charged one-electron ions in excellent agreement with the analytically known Dirac energies.

Since it is desirable to have an unambiguous and well-defined relativistic Douglas–Kroll–Hess method at hand, we may recommend the use of either the fourth-order DKH4 Hamiltonian or the infinite-order scheme as suitable DKH models. The reasons for this recommendation are twofold: First, the fourth-order Hamiltonian is the highest even order not depending on the chosen parameterization of the unitary matrices.⁸ Second, though the dependence on the parametrization, which shows up in the fifth- and all higher-order Hamiltonians, is small, it is diminished only in the infinite-order limit, which makes the very high DKH orders attractive from a puristic point of view. Following this philosophy, a recent implementation of the two-component Douglas–Kroll–Hess method has been carried out up to fourth-order DKH4.¹⁷

The present implementation comprises a scalar-relativistic version of the Douglas–Kroll–Hess method, but due to the modular and symbolic character of the code it is straightforward to extend the implementation to the two-component domain. In future work, we will discuss the calculation of molecular properties within the arbitrary-order DKH scheme, the inclusion of spin–orbit terms and the transformation of the electron–electron interaction potentials. For the latter, it will be very useful to fall back on recent results obtained by Boettger¹⁸ and by Majumder, Matveev, and Rösch¹⁶ in order to arrive at efficient implementations which can compete with four-component methods. Work in these directions is currently in progress in our laboratory.

ACKNOWLEDGMENT

This work has been financially supported by the Deutsche Forschungsgemeinschaft (DFG) via the Schwer-

punktprogramm SPP 1145 “Modern First-Principles Methods” (Re 1703/1-1).

- ¹M. Reiher and A. Wolf, J. Chem. Phys. **121**, 2037 (2004).
- ²M. Barysz, A. J. Sadlej, and J. G. Snijders, Int. J. Quantum Chem. **65**, 225 (1997).
- ³M. Barysz, J. Chem. Phys. **114**, 9315 (2001).
- ⁴M. Barysz and A. J. Sadlej, J. Chem. Phys. **116**, 2696 (2002).
- ⁵D. Kędziera and M. Barysz, Chem. Phys. Lett. **393**, 521 (2004).
- ⁶B. A. Hess, Phys. Rev. A **33**, 3742 (1986).
- ⁷G. Jansen and B. A. Hess, Phys. Rev. A **39**, 6016 (1989).
- ⁸A. Wolf, M. Reiher, and B. A. Hess, J. Chem. Phys. **117**, 9215 (2002).
- ⁹T. Nakajima and K. Hirao, J. Chem. Phys. **113**, 7786 (2000).
- ¹⁰T. Nakajima and K. Hirao, Chem. Phys. Lett. **329**, 511 (2000).
- ¹¹A. Wolf, M. Reiher, and B. A. Hess, in *Relativistic Electronic Structure Theory (Part I)*, edited by P. Schwerdtfeger, Series: Theoretical and Computational Chemistry (Elsevier, New York, 2002), pp. 622–663.
- ¹²C. van Wüllen, J. Chem. Phys. **120**, 7307 (2004).
- ¹³C. van Wüllen, Chem. Phys. (in press).
- ¹⁴M. Mayer, S. Krüger, and N. Rösch, J. Chem. Phys. **115**, 4411 (2001).
- ¹⁵A. Matveev and N. Rösch, J. Chem. Phys. **118**, 3997 (2003).
- ¹⁶S. Majumder, A. V. Matveev, and N. Rösch, Chem. Phys. Lett. **382**, 186 (2003).
- ¹⁷J. E. Peralta and G. E. Scuseria, J. Chem. Phys. **120**, 5875 (2004).
- ¹⁸J. C. Boettger, Phys. Rev. B **62**, 7809 (2000).
- ¹⁹T. Nakajima and K. Hirao, J. Chem. Phys. **119**, 4105 (2003).
- ²⁰M. Douglas and N. M. Kroll, Ann. Phys. (N.Y.) **82**, 89 (1974).
- ²¹R. McWeeny, Rev. Mod. Phys. **32**(2), 335 (1960).
- ²²A. Wolf and M. Reiher, Phys. Rev. A (to be published).
- ²³P. J. Mohr and B. N. Taylor, Rev. Mod. Phys. **72**, 351 (2000).
- ²⁴G. L. Malli, A. B. F. Da Silva, and Y. Ishikawa, Phys. Rev. A **47**, 143 (1993).
- ²⁵C. C. J. Roothaan and P. S. Bagus, in *Methods in Computational Physics. Quantum Mechanics, Vol. 2*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, NY, London, 1963), pp. 47–94.
- ²⁶L. Visscher, O. Visser, P. J. C. Aerts, H. Merenga, and W. C. Nieuwpoort, Comput. Phys. Commun. **81**, 120 (1994).
- ²⁷A. Wolf, M. Reiher, and B. A. Hess, J. Chem. Phys. **120**, 8624 (2004).