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A two-centre implementation of the Douglas–Kroll transformation in relativistic calculations

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Abstract

An implementation of the Douglas–Kroll (DK) transformation is described within a new relativistic quantum chemistry code, MAGIC, which performs calculations on systems containing heavy atoms. This method reduces the computational cost in terms of memory requirements that are associated with completeness identities in the DK implementation by factorizing the one-electron matrices into smaller ones that depend only on two atoms at a time. Examples are presented. © 1998 Elsevier Science B.V.

1. Introduction

The consideration of relativistic effects is essential to the proper understanding of the chemistry of heavy elements ($Z > 80$), in particular the actinides [1], which form a major focus for the nuclear industry. The MAGIC quantum chemistry code, newly developed, is directed at providing a means of performing chemically accurate calculations on systems containing many atoms, some of which are heavy. The MAGIC code is described elsewhere [2], but, in its essentials, it is a code based on the use of Gaussian basis sets that allows density functional calculations within the Kohn–Sham paradigm. The Coulomb integrals are evaluated by the Rys quadrature [3], and an auxiliary basis set is used, according to the method of Dunlap [4], and Eichkorn et al. [5].

In addition to the standard, non-relativistic all electron scheme, relativistic effects are considered by an implementation of the effective core potentials (ECP) of Kahn, Baybutt and Truhlar [6]. Alternatively, the relativistic methods of Douglas and Kroll (DK) [7] or Chang, Pelissier and Durand (CPD) [8] can be used. There is no claim here that any of the methods that have been implemented within MAGIC are new. The only distinct feature is that the code was written with these concepts in mind, unlike, for example, many of today's density functional codes that have their origins in standard Hartree–Fock self-consistent Gaussian codes. All the code has been written from scratch, and, as it has been developed, some minor improvements, such as the one described in this Letter, have been implemented.

We must of course reference some of the many calculations that have been made using two-component relativistic codes. Specifically, we refer to calculations using the Amsterdam density functional code [9], using the CPD Hamiltonian [10] from the

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work of Baerends, and several calculations using the DK transformation [11]. ECP calculations have, of course, been in existence for many years, but they are not relevant to this particular study.

The starting point for relativistic calculations is the Dirac equation

$$h^{\mathrm{D}}\Psi=\left(c\boldsymbol{\alpha}\cdot\boldsymbol{\pi}+V+mc^2(\beta-1)\right)\Psi=E\Psi, \tag{1}$$

where $\boldsymbol{\alpha}$, $\boldsymbol{\pi}$, β are defined in the standard manner [12,13].

The four-component wavefunction, Ψ, is written as a pair of two-spinors

$$\Psi=\begin{pmatrix}\Psi_{\mathrm{L}}\\ \Psi_{\mathrm{S}}\end{pmatrix}, \tag{2}$$

where Ψ_{L} is the large component and Ψ_{S} the small component. Without considering quantum electrodynamics, the transition to a many electron calculation is made by adding the Coulomb operator to the Dirac Hamiltonian, giving the Dirac–Coulomb Hamiltonian.

$$H_{\mathrm{DC}}=\sum_i h_i^{\mathrm{D}}+\sum_{i<j}\frac{1}{r_{ij}} \tag{3}$$

This can be corrected for retardation of the potential by the addition of the Gaunt and Breit corrections [14], if necessary. For practical chemical applications the Dirac–Coulomb Hamiltonian has the disadvantage that the ‘small’ and ‘large’ spinors are coupled, complicating the solution of the equation of motion with no real benefit since the small spinor, describing the positronic part of the electronic wavefunction, is of little chemical significance.

This study is based on the use of the DK method, in an approach which avoids large storage requirements. Section 2 briefly summarises the DK method. Section 3 presents the problem of the completeness of the basis set in the resolution of the identity, and Section 4 develops a method to overcome this problem. Finally in Section 5 some results are presented.

2. The Douglas–Kroll method

A number of methods in which the large and small spinors are decoupled (up to some order) have been introduced, starting with the work of Fouldy and Wouthysen (FW) [15]. This allows the part of the Hamiltonian dealing with the small component to be treated approximately, giving rise to an effective one-spinor equation, the solution of which is amenable to the usual techniques of quantum chemistry. Since the transformation is applied to the Dirac Hamiltonian, the practical benefit is a modified one-electron Hamiltonian containing terms expected on physical grounds, namely the spin-orbit operator.

One such transformation is that introduced by Douglas and Kroll and subsequently adapted for use in the normal quantum chemistry paradigm by Hess [12,13,16–18]. This is briefly summarised below.

In a FW transformation the Dirac Hamiltonian is transformed

$$Uh^{\mathrm{D}}U^{-1}\Psi\equiv UEU^{-1}\Psi=E\Psi. \tag{4}$$

In general a single unitary transformation is insufficient to separate totally the small and large components of the wavefunction, and a separation only up to certain order in a chosen parameter is achieved. Repeated application of the unitary transformation can decouple the wavefunction to any desired order. Following Hess we define the even operator, $\mathscr{E}$, which couples the large components with the large ones and the small components with the small ones, and the odd operator, $\mathscr{O}$, which couples the large with the small components This definition is equivalent to

$$[\beta,\mathscr{E}]=0, \tag{5}$$

$$[\beta,\mathscr{O}]_+=0. \tag{6}$$

With this notation the Dirac Hamiltonian can be written

$$\begin{aligned}h^{\mathrm{D}}&=c\boldsymbol{\alpha}\cdot\boldsymbol{\pi}+V+mc^2(\beta-1)\\ &\equiv mc^2\beta+\mathscr{E}+\mathscr{O}.\end{aligned} \tag{7}$$

In the absence of an external magnetic field, a free particle FW transformation is applied to the Dirac Hamiltonian. The transformation has the unitary operator

$$U_0=A(1+\beta R), \tag{8}$$

$$U_0^{-1}=(R\beta+1)A, \tag{9}$$

where

$$A = \left(\frac{E_\pi + mc^2}{2E_\pi} \right)^{1/2}, \tag{10}$$

$$R = c\frac{\boldsymbol{\alpha} \cdot \boldsymbol{\pi}}{E_\pi + mc^2}, \tag{11}$$

$$E_\pi = (c^2\boldsymbol{\pi}^2 + m^2c^4)^{1/2}. \tag{12}$$

Working in a momentum space representation, so that E_π is diagonal, and using the commutator results above, gives the transformed Hamiltonian

$$h_1^{\mathrm{D}} = U_0 h^{\mathrm{D}} U_0^{-1} = \beta E_\pi + \mathscr{E}_1 + \mathscr{O}_1, \tag{13}$$

where the new operators are

$$\mathscr{E}_1 = A(V + RVR)A, \tag{14}$$

$$\mathscr{O}_1 = \beta A(RV - VR)A. \tag{15}$$

To further decouple the large and small component, Douglas and Kroll [7] applied the unitary transformation

$$U_1 = (1 + W^2)^{1/2} + W, \tag{16}$$

where W is anti-Hermitian (for the complete definition of W see Ref. [7]). We do not enter into the details of the further expansions (for which the reader can see the original work by Hess [12,13]), but we only report the final expression of h^{DK}

$$h^{\mathrm{DK}} = U_1 h_1^{\mathrm{D}} U_1^{-1} = \beta E_\pi + \mathscr{E}_1 + [W, \mathscr{O}_1] + \tfrac{1}{2}[W^2, \beta E_\pi]_+ + W\beta E_\pi W, \tag{17}$$

where terms correct to second order in the potential contain no coupling between large and small components.

In the DK method there are alternative ways of treating the inter-electronic effects, either by leaving untransformed the Coulomb potential and exchange-correlation potential [16], or by transforming the two-electron potential [13,19]. In the present implementation we used untransformed Coulomb and exchange-correlation potential.

3. Introduction of a basis set

In the case in which an external vector potential is not considered, $\boldsymbol{\pi}$ will be replaced by $\boldsymbol{p}$, and moving into the chemical scale by subtracting mc^2, the final one-spinor DK Hamiltonian is obtained

$$h^{\mathrm{DK}} = E_p + V'_{\mathrm{ext}} + V_{\mathrm{Coul}} + V_{\mathrm{XC}} - mc^2 \tag{18}$$

where E_p is defined by Eq. (12), and

$$V'_{\mathrm{ext}} = A[V_{\mathrm{ext}} + RV_{\mathrm{ext}}R]A + WE_pW + \tfrac{1}{2}W^2E_p + \tfrac{1}{2}E_pW^2. \tag{19}$$

The molecular calculations require the elements of the Fock operator between basis functions. For the calculation of the matrix elements for V_{Coul} and V_{XC} we proceed as in a standard density functional program. The calculation of the other elements of the Kohn–Sham matrix, E_p and V'_{ext}, are more complicated because of the presence of the square root in the definitions of E_p and A. These elements are computed by transforming to a momentum space representation and calculating the matrix elements of the operators on the diagonal. The calculation of the matrix form of the operators in such a way requires frequent resolution of the identity and the results of the calculations are thus dependent on the quality of the basis set.

The one-electron terms can be collected

$$T^{\mathrm{DK}} = E_p - mc^2 + AV_{\mathrm{ext}}A + ARV_{\mathrm{ext}}RA + WE_pW + \tfrac{1}{2}\left(W^2E_p + E_pW^2\right) \tag{20}$$

Since only the one-electron potential has been transformed, the DK Kohn–Sham matrix is formed by replacing $T + V_{\mathrm{ext}}$ with

$$T^{\mathrm{DK}} = E_p - mc^2 + V'_{\mathrm{ext}} \tag{21}$$

For the usual application in quantum chemistry we work with a finite basis function space. The transition from basis function space to momentum space is effected by diagonalizing the basis function representation of the kinetic energy ($m = 1$ in atomic units)

$$p^2 = 2D^{\mathrm{T}}TD, \tag{22}$$

where p is diagonal in a discrete momentum basis. This transformation is exact only to the extent that the set of basis functions is complete. Since p is diagonal the matrix representations of E_p, A and R can readily be formed and thus T^{DK} formed by matrix multiplication: completeness of the basis is again required.

This method, if naively implemented, has large storage requirements since, for efficiency, the elements of the matrices involved in the DK transformation are all held in memory. This problem is exacerbated because, as proposed by Hess, the momentum functions are calculated in the primitive basis function space. This improves the resolution of the identity without requiring the use of a specially chosen basis set (as has been alternatively proposed), but at the cost of significantly increasing the effective size of the basis set for the large systems considered.

4. The two-centre approximation

The subroutine that performs the DK transformation is outlined as follows. S and T denote the overlap and kinetic matrix respectively in the primitive space.

1. The matrix $S^{-1/2}TS^{1/2}$ is diagonalised to give the momentum eigenvectors k_i and eigenvalues p_i^2.
2. The diagonal matrix E_p is constructed in momentum space and its contribution to the Kohn–Sham matrix $\sum_i \langle \alpha | k_i \rangle E_{p_i} \langle k_i | \beta \rangle$ evaluated.
3. V_{ext} is calculated in the primitive basis, and transformed to the momentum basis. The matrix $AV_{\text{ext}}A$ is then calculated in this basis, and its contribution to the Kohn–Sham matrix is evaluated as above.
4. To evaluate the term $ARV_{\text{ext}}RA$, the matrices $pV_{\text{ext}}p$ have to be calculated. These are calculated from standard one-electron integral Gaussian routines. Their contribution to the Kohn–Sham matrix is then evaluated as in step 3.
5. The remainder term is computed from $AV_{\text{ext}}A$, $ARV_{\text{ext}}RA$, E_p and p^2, and its contribution to the Kohn–Sham matrix is evaluated as above.

When systems containing many atoms are studied, the use of large primitive basis sets, necessary for the resolution of the identity, becomes unpractical. Here a method that overcomes this problem is presented. The basic idea is that the matrix elements of the one-electron terms of the Hamiltonian are computed within the set of basis functions of two atoms at a time. The method is therefore referred as the two centre (TC) approximation. This follows from [9], in which a similar approach was used in the evaluation of Coulomb integrals using auxiliary functions.

In the general approach, the matrices appearing in the one-electron term, T^{DK}, are computed for the whole system. The dimensions of these matrices therefore depend on the number of primitive basis functions on all the atoms. Within the TC method, the matrices are computed only for two centres (or atoms) at a time. In this way the number of atoms is no longer a limiting factor.

The TC method is, of course, applicable to the calculation of the matrix elements of any operator. In the case of the DK transformation we have implemented it as follows. Consider the kinetic matrix, T. For every pair of atoms (a,b) we extract the submatrices T_{aa}, T_{ab}, T_{ba} and T_{bb}, where for example, T_{ab} is a matrix comprising the elements

$$\left\{ \left\langle \chi_\alpha^a | T | \chi_\beta^b \right\rangle \right\}_{\alpha\beta}, \tag{23}$$

where the superscript indicates the center on which the primitive lies and α, β denote the primitives. From this we construct the block 2×2 square matrix

$$\begin{pmatrix} \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & T_{aa} & \cdots & T_{ab} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & T_{ba} & \cdots & T_{bb} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix} \rightarrow \begin{pmatrix} T_{aa} & T_{ab} \\ T_{ba} & T_{bb} \end{pmatrix}. \tag{24}$$

This is repeated for the nuclear attraction matrix, V, and the other quantities required for the DK transformation. The standard DK transformation routine, as described above, is now applied to these matrices. This produces a T^{DK} that can be written with the same structure

$$\begin{pmatrix} T_{aa}^{\text{DK}} & T_{ab}^{\text{DK}} \\ T_{ba}^{\text{DK}} & T_{bb}^{\text{DK}} \end{pmatrix} \rightarrow \begin{pmatrix} \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & T_{aa}^{\text{DK}} & \cdots & T_{ab}^{\text{DK}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \\ \cdots & T_{ba}^{\text{DK}} & \cdots & T_{bb}^{\text{DK}} & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{pmatrix}. \tag{25}$$

The blocks of this matrix are now added into the full T^{DK} matrix according to the centre labels. This is repeated for every unique pair of atoms, thereby building up the total matrix as a sum of pairwise terms.

Let us consider a system containing N centres, the dimension of the primitive matrices (stored as lower triangles, since they are symmetric) being $\frac{1}{2}M_{\mathrm{TOT}}(M_{\mathrm{TOT}}+1)$, where M_{TOT} is the total number of unique primitives in the whole system. With the matrix factorization the dimension of the matrices reduces to $\frac{1}{2}M_{AB}(M_{AB}+1)$, where M_{AB} is the total number of unique primitives on centres A and B. For each pair of centres the factorization is obtained by a two-loop scheme, inside which the lower triangle of the one-electron matrices of dimension M_{AB} are computed.

As already said, the TC approximation implies considerable memory savings, especially when large systems are treated. Let us suppose that the number of primitive functions, M, is the same for each atom. In the general approach the dimension of the one-electron matrices is of order of magnitude $O((N \cdot M)^2)$, while with the TC approximation it reduces to $O((2 \cdot M)^2)$. Note also that the dimension of the primitive set on each atom can be extended arbitrarily in the TC case to improve the resolution of identities.

5. Applications

Before checking the efficiency of the TC approximation, we first examined if it significantly changed the values of the computed energies. We thus compared the absolute energies for a series of test molecules obtained with the standard DK transformation using the full primitive set and the TC approximation. The calculations were done using the LDA functional [20,21]. For the radial quadrature we followed the scheme by Mura et al. [22], and for the angular one the scheme by Lebedev [23]. Various standard basis sets were used. In Table 1 we report the number and type of polarized functions and their exponents, present in each basis set. Standard auxiliary basis sets [5] were placed on the centres of all the molecules.

Table 1
Exponents of the polarization functions used in the calculations

Atom	Basis set	p	d	f
H	p-VDZ	0.727		
	p-VTZ	1.057		
	p-VTZ	1.057		
	p-VTZ	1.057		
C	5s4p2d		1.200	
			0.400	
	8s6p3d		1.800	
			0.600	
			0.200	
O	5s4p2d		1.350	
			0.450	
	8s6p3d		2.700	
			0.900	
			0.300	
N	3-21G *		0.800	
Si	p-VDZ		0.275	
P	p-VDZ		0.373	
	p-VTZ		0.216	0.452
			0.652	
	9s6p1d		1.990	
S	p-VDZ		0.479	
Cl	p-VDZ		0.600	

In Table 2 we report for each molecule the energy obtained with the standard DK method and the difference between this value and that obtained with the TC approximation. We observe that the energy difference is lower than 10^{-6} E_{h} for diatomic molecules (this arises because in the TC approximation Kohn–Sham matrix elements for basis functions on a given centre only use the primitives on that centre). When molecules with three or more centres are treated, the energy difference varies in between 10^{-6} and 10^{-4} E_{h}. The energy-difference increase, in going from smaller to larger systems, is due to the fact that the TC approximation does not include the effects of the primitives on the other centres. We also observe that the energy difference decreases if we increase the quality of the basis set.

We also performed calculations on linear hydrocarbons of type C_nH_{n+2} ($n = 6$, 10, 14, 18, 22, 26), using a DZP basis set. In Fig. 1 we report the energy difference between the two methods as a function of the number of carbon atoms, n. Even for the two largest molecules ($n = 22$, 26), the energy difference is still of the order of 10^{-4} E_{h}. The decrease in going from $C_{22}H_{24}$ to $C_{26}H_{28}$ is attributed to a

Table 2
All electron relativistic energies (E) of molecules calculated with the DK method using the full primitive set, and differences (D_E) between these energies and those computed with a two centre primitive set (TC) in the completeness identities. The value of D_E is not reported when it is lower than the convergence threshold (10^{-6} E_h). When only one basis set is indicated, it refers to all the atoms of the systems. In the two PH_3 cases, the two basis sets reported refer to P and H respectively. Note that the TC energies are always higher than those obtained without using the approximation

Molecule	Basis set	E / E_h	$D_E / 10^{-3}$ E_h
N_2	3-21G*	−107.352972	–
BN	DZ	−77.919363	–
CO	DZ	−111.657119	–
CCl	DZ	−497.582636	–
CCl_2O	DZ	−952.621629	0.144
Cl_2S	p-VDZ	−1318.802537	0.058
$SiClH_3$	DZ	−750.668367	0.048
	p-VDZ	−750.572051	0.044
PH_3	DZ	−342.306352	0.024
	DZP	−342.344175	0.059
	p-VDZ	−342.289492	0.025
	p-VTZ	−342.395794	0.016
	9s6p, 3s2p	−342.286053	0.068
	9s6p1d, 6s3p	−342.301175	0.266
CO_2	DZ	−185.936882	0.010
	DZP	−186.030825	0.013
	5s4p	−186.016546	0.004
	5s4p2d	−186.110967	0.002
	8s6p	−186.011746	0.009
	8s6p3d	−186.104914	0.005

structural rearrangement, arising from a change in the assumed geometry, which was obtained using the forcefield by Rappe et al. [24].

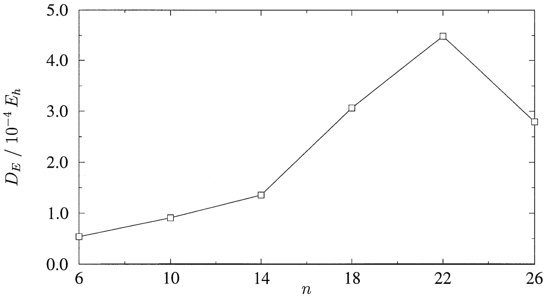

Fig. 1. Difference ($D_E / 10^{-4}$ E_h) between the DK relativistic energies computed using the full primitive set and the TC approximation, as a function of the number of carbon atoms, n, in the compounds C_nH_{n+2} ($n = 6,10,14,18,22,26$). Note that the TC energies are higher than the full energies.

6. Conclusions

The matrices that occur in the DK transformation have been decomposed into two-centre pairs, giving the TC method. This approach has been shown to allow calculations on larger systems, by reducing the memory requirements, without significant loss of accuracy. The approach can be used to partition other matrix quantities with equivalent benefits.

This Letter used the new program MAGIC designed for computational chemistry calculations on molecules containing heavy atoms. In forthcoming publications we shall give more details of MAGIC, and applications which are relevant to heavy atom chemistry.

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References

[1] P. Pyykkö, Chem. Rev. 88 (1988) 563.
[2] A. Willetts, A.M. Simper, L. Gagliardi, A.G. Ioannou, C.-K. Skylaris, S. Spencer, N.C. Handy, to be submitted.
[3] J. Rys, M. Dupuis, H.F. King, J. Comput. Chem. 4 (1983) 154.
[4] B.I. Dunlap, J.W.D. Connolly, J.R. Sabin, J. Chem. Phys. 71 (1979) 3396.
[5] K. Eichkorn, O. Treutler, H. Öhm, M. Häser, R. Ahlrichs, Chem. Phys. Lett. 240 (1995) 283.
[6] L.R. Kahn, P. Baybutt, D.G. Truhlar, J. Chem. Phys. 65 (1976) 3826.
[7] M. Douglas, N.M. Kroll, Ann. Phys. 82 (1974) 89.
[8] C. Chang, M. Pellissier, P. Durand, Physica Scripta 34 (1986) 394.
[9] E.J. Baerends, D.E. Ellis, P. Ros, Chem. Phys. 2 (1973) 42.
[10] E.M. Wezenbeek, E.J. Baerends, T. Ziegler, Inorg. Chem. 34 (1995) 238.
[11] O.D. Haberlen, S.-C. Chung, N. Rosch, Int. J. Quantum Chem.: Quantum Chem. Symp. 28 (1994) 595.
[12] B.A. Hess, Phys. Rev. A 32 (1985) 756.
[13] B.A. Hess, Phys. Rev. A 33 (1986) 3742.
[14] G. Breit, Phys. Rev. 39 (1932) 616.
[15] L.L. Foldy, S.A. Wouthysen, Phys. Rev. 78 (1950) 29.
[16] G. Jansen, B.A. Hess, Phys. Rev. A 39 (1989) 6016.

[17] R. Samzow, B.A. Hess, Chem. Phys. Lett. 184 (1992) 491.
[18] R. Samzow, B.A. Hess, G. Jansen, J. Chem. Phys. 96 (1992) 1227.
[19] C. Park, J.E. Almlöf, Chem. Phys. Lett. 231 (1994) 269.
[20] P.A.M. Dirac, Proc. Cambridge Philos. Soc. 26 (1930) 376.
[21] S.H. Vosko, L. Wilk, M. Nusair, Canad. J. Phys. 58 (1980) 1200.
[22] M.A. Mura, P. Knowles, J. Chem. Phys. 104 (1996) 9848.
[23] V.I. Lebedev, in: S. Sobolev (Ed.), Proceedings of the conference on differential equations in numerical mathematics, Novosibirsk, 1980, Nauka.
[24] A.K. Rappe, C.J. Casewit, K.S. Colwell, W.A. Goddard-III, W.M. Skiff, J.Am. Chem. Soc. 114 (1992) 10024.