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On the eigenfunctions of the Douglas–Kroll operator

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Dedicated to Prof. Werner Kutzelnigg at the occasion of his 75th birthday.

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ABSTRACT

The matrix elements of the quasirelativistic Douglas–Kroll operators up to the fourth order for hydrogen-like ions is constructed with as few additional approximations as possible, to investigate the behaviour of its 1s eigenfunctions in the vicinity of the nucleus. Because Douglas–Kroll is a momentum space theory, we use a basis set of spherical waves which are eigenfuntions of the square of the momentum operator. While this avoids the most serious approximation of the standard Douglas–Kroll–Hess protocol, namely that the basis functions used to construct the Douglas–Kroll operator are eigenfunctions of the (squared) momentum operator, it also makes the convergence of this expansion very slow, because spherical waves are not well suited to represent the (weak) singularities of the eigenfunctions at the position of the point-like nucleus. On the other hand, the convergence is quite monotonic, and information on the behaviour close to the nucleus can be extracted from the convergence rate. Starting with the second-order, the eigenfunctions of the Douglas–Kroll operator are not "more singular" than the Dirac eigenfunctions, and the occurence of an additional error when using regular basis sets, as postulated in the literature, can not be observed. The resolution of the identity, which is involved in any practical approach to construct the matrix elements of the Douglas–Kroll operators beyond the first order, is a minor problem for heavy nuclei.

1. Introduction

For a long time, relativistic quantum chemistry has been dominated by the so-called quasirelativistic methos. In these methods, the charge conjugation degrees of freedom are removed from the Dirac equation, thus giving birth to a theory "for electrons only" [1]. Because the negative-energy branch of the Dirac spectrum is removed, quasirelativistic operators are (mostly) variationally stable, and for many applications the reduced complexity from four to two components leads to a reduction of the computational effort, although the implementation of two-component methods is often more complicated than in the so-called "fully relativistic", that is, four-component case. Another attractive feature of quasirelativistic methods is that they generate a separation into scalar-relativistic and spin–orbit effects, which is very useful to rationalize trends of relativistic effects across the periodic table of the elements. Note that such a separation is not unique [2], but different for each quasirelativistic method. For a qualitative discussion of trends this seems not to be a problem, but for close comparisons of different quasirelativistic methods it has been observed that for scalar-relativistic results the differences are somewhat larger than if the results including spin–orbit coupling are compared [3].

The majority of quantum chemical software uses a basis set expansion for the atomic or molecular orbitals. Only the matrix elements of the quasirelativistic operator with the basis functions enter such a calculation, and it is largely immaterial how they are generated. While the traditional approach, at least in principle, starts from the construction of a quasirelativstic operator, an alternative approach starts from the matrix elements of the Dirac operator and generates matrix element of a not fully specified quasirelativistic operator at matrix level, that is, within the finite dimensional framework established by the matrix representation of the Dirac operator. This approach somewhat lingered around in the literature [4–7] and has recently more explicitly been advocated by Kutzelnigg and Liu [8,9]. Likewise, the Douglas–Kroll approach [10–12], which has originally been formulated as a theory for a quasirelativistic operator, has also been used to generate exact quasirelativistic theories at matrix level[13–15].

These theories are more or less equivalent since they start from the Dirac operator projected onto a finite-dimensional subspace which is defined by the basis set used to expand the large components and the restricted kinetic balance condition. For this finite-dimensional operator, the spectral representation is easily accessible via a matrix diagonalization. This diagonalization is either performed explicitly (in the one-step procedures) or iteratively. Whether this make theories using quasirelativistic operators obsolete, as sometimes claimed [9], remains to be seen. An argument central to this verdict is that eigenfunctions of approximate quasirelativistic operators are "more singular" than the Dirac solutions, and that even if an exact quasirelativistic operator were readily available additional errors (not present in a four-component formalism) will occur if it is used with regular basis functions [16].

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In this line of argument, the success of the Douglas–Kroll method is explained as a consequence of the fact that all known implementations so far are based on matrix operations, and that the Douglas–Kroll transformation at operator level gives quasirelativistic operators which are much more unpleasant than usually believed [16].

There are only few analytical results on the properties of Douglas–Kroll operators. Hardekopf and Sucher have found that the eigenfunctions of the first-order Douglas–Kroll ($DK1$) operator are more singular than the Dirac eigenfunctions [17], such that this operator has no solutions for point-like nuclei with $Z > 124$ in contrast to the Dirac equation, which has solutions up to $Z = 137$. More recently, Brummelhuis et al. [18] have proven that the second-order Douglas–Kroll operator ($DK2$) *does* have solutions up to $Z = 137$. No analytical results are available beyond $DK2$.

Within a given finite basis set, numerical high-order Douglas–Kroll results can match the Dirac values (in that basis set) to any desired accuracy [19,20], but this may not give information about the “true” spectrum of the Douglas–Kroll operators. The present author has recently given Douglas–Kroll results up to the sixth order [21] obtained with a very large Gaussian basis set and claimed that these results match the eigenvalues to microhartree accuracy. From this data, it has been extracted that the leading error of the 6th order Douglas–Kroll ($DK6$) 1s eigenvalue for hydrogen-like ions is $\mathcal{O}(Z^{10}c^{-8})$, ($Z$ is the nuclear charge, and c the speed of light) in contrast to the claim [16] that only the leading relativistic correction $\mathcal{O}(Z^4c^{-2})$ can be correct if one uses quasirelativistic operators. This discrepancy calls for clarification. To do so, the Douglas–Kroll method was implemented for a basis set of spherical waves, which removes the most critical approximation underlying all Douglas–Kroll implementations reported so far.

Since atomic nuclei are extended and a large part of relativistic molecular structure calculations performed today use finite nuclear models, one may ask whether the question how Douglas–Kroll eigenfunctions behave close to a point charge is actually relevant. However, although an extended nucleus removes all singularities in a mathematical sense, these still raise their head through the dependence of the results on the chosen nuclear model. Therefore, knowing what happens in the limit of a point-charge nucleus is still important.

2. The Douglas–Kroll Hamiltonian in a spherical wave basis

The Douglas–Kroll method, including higher orders, is well documented in the literature [14,20,22–25] and only those aspects important in the present context will be covered here. For the purpose of this presentation it is sufficient only to consider hydrogenic atomic ions for which the external potential in which the electron moves is spherical, $V(r) = -\frac{Z}{r}$. One starts applying the exact Foldy–Wouthuysen transformation for a free particle to this bound-electron Dirac operator $\mathbf{H}_D$

$$\mathbf{H}_D^{(1)} = \mathbf{U}^{(0)}\mathbf{H}_D\mathbf{U}^{(0)\dagger} = \begin{pmatrix} E_0 + E_1 & O_1 \\ O_1^\dagger & -E_0 + E_1 \end{pmatrix} \tag{1}$$

$$\mathbf{U}^{(0)} = \begin{pmatrix} A & AR \\ -AR & A \end{pmatrix} \tag{2}$$

with the two-component operators E_0, A, R given by

$$A = \sqrt{\frac{E_0 + mc^2}{2E_0}}, \quad E_0 = \sqrt{\vec{p}^2c^2 + m^2c^4}, \quad R = \frac{c\vec{\sigma}\vec{p}}{E_0 + mc^2} \tag{3}$$

and

$$E_1 = AVA + ARVRA, \quad O_1 = ARVA - AVRA. \tag{4}$$

This transformation does not bring the Dirac operator to a block-diagonal form, the remaining off-diagonal blocks O_1 are first order in the external potential, $O_1 \sim Z^1$. Subsequent transformation steps yield $\mathbf{H}_D^{(2)}, \mathbf{H}_D^{(3)}, \ldots$, and in $\mathbf{H}_D^{(k)}$ the off-diagonal blocks are further reduced to $\sim Z^k$. This sequence eventually converges to a block-diagonal operator whose diagonal elements are now given, by construction, as a power series in Z: in the diagonal blocks of $\mathbf{H}_D^{(k)}$, the terms up to $\mathcal{O}(Z^{2k-1})$ are not changed in the subsequent transformation steps, such that each step gives two more coefficients of an expansion of an exact block-diagonal operator in powers of Z.

Going from a four-component description which is symmetric w.r.t. charge conjugation to a two-component formalism for the positive-energy states only, one usually subtracts the rest energy mc^2 from the diagonal blocks, and then the first- and second-order Douglas–Kroll operators are

$$H_{DK1} = (E_0 - mc^2) + E_1 \tag{5}$$

$$H_{DK2} = H_{DK1} + \frac{1}{2}(W_1O_1 + O_1W_1) \tag{6}$$

Note that other names are in also use for H_{DK1}. W_1 is the solution of the operator equation

$$W_1E_0 + E_0W_1 = O_1. \tag{7}$$

The expressions for the higher-order DK operators can be found in the literature. Their derivation is tedious but much effort can be delegated to computer algebra systems [23]. At this point we also mention a quasirelativistic operator which one obtains if one adds the potential to the relativistic kinetic energy

$$H_{RK} = (E_0 - mc^2) + V \tag{8}$$

(RK stands for ‘relativistic kinematics’). This is an operator for a spinless particle which is lacking, for example, the spin–orbit interaction. It has been discussed a while ago [26] but apparently not found much use. We mention this operator since the eigenfunctions both of H_{DK1} and H_{RK} are “more singular” than the Dirac eigenfunctions [17,27,28], bound-state solutions for point-charge nuclei exist for H_{DK1} only up to $Z = 124$ and for H_{RK} only up to $Z = 87$.

This theory is sometimes called a momentum space theory because the basic operators R, A, and E_0 are local in momentum space. In real space only their action on eigenfunctions of $\vec{p}^2$ is defined. If we had such (normalized and orthogonal) two-component basis functions Ω_i with $\vec{p}^2\Omega_i = k_i^2\Omega_i$, then the matrix elements of our basic operators are well defined, for example

$$\langle\Omega_i|E_0|\Omega_j\rangle = \epsilon_i\delta_{ij} \tag{9}$$

$$\langle\Omega_i|E_1|\Omega_j\rangle = a_ia_j\langle\Omega_i|V|\Omega_j\rangle + a_ia_jr_ir_j\langle\Omega_i|\vec{\sigma}\vec{p}V\vec{\sigma}\vec{p}|\Omega_j\rangle \tag{10}$$

$$\langle\Omega_i|O_1|\Omega_j\rangle = a_ia_jr_i\langle\Omega_i|\vec{\sigma}\vec{p}V|\Omega_j\rangle - a_ia_jr_j\langle\Omega_i|V\sigma\vec{p}|\Omega_j\rangle \tag{11}$$

with

$$\epsilon_i = \sqrt{k_i^2c^2 + m^2c^4}, \quad a_i = \sqrt{\frac{\epsilon_i + mc^2}{2\epsilon_i}}, \quad r_i = \frac{c}{\epsilon_i + mc^2} \tag{12}$$

Furthermore, the anticommutator relation Eq. (7) can be inverted exactly in such a basis, and one finds for the matrix elements of W_1

$$\langle\Omega_i|W_1|\Omega_j\rangle = \frac{\langle\Omega_i|O_1|\Omega_j\rangle}{\epsilon_i + \epsilon_j}. \tag{13}$$

While the matrix elements of H_{DK1} can be evaluated exactly in such a basis, one approximation cannot be avoided beyond first-order Douglas–Kroll: for H_{DK2}, one needs matrix elements of the product W_1O_1 but one only has matrix elements of the two factors W_1 and O_1. This is where a resolution of the identity (RI approximation) comes in, and one *approximates*

$$\langle\Omega_i|W_1O_1|\Omega_j\rangle \approx \sum_l\langle\Omega_i|W_1|\Omega_l\rangle\langle\Omega_l|O_1|\Omega_j\rangle \tag{14}$$

All numerical Douglas–Kroll results reported so far follow the protocol of Hess [29,30]. In most cases finite Gaussian basis sets