Brief Reports

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Revision of the Douglas-Kroll transformation

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A revision of the Douglas-Kroll transformation showed that the sign of the second-order term in the resulting transformed Dirac Hamiltonian has to be changed. This is in accordance with its use in practical applications. A brief review of the theory is given and a slight simplification of the second-order term is presented.

In 1974 Douglas and Kroll[1] published a method that allows for decoupling of the upper and lower components of a Dirac spinor in the presence of an external potential. Their method consists of a series of transformations leading to an expansion of the Dirac Hamiltonian in orders of the external potential and thus in powers of the coupling constant. Every consecutive transformation removes the lowest-order odd term, so that the decoupling is possible to any desired order of the coupling constant. The purpose of this Brief Report is the correction of a sign error in one of the terms beyond the free-particle Foldy-Wouthuysen transformation. Douglas and Kroll's derivation is repeated here somewhat more explicitly in order to show the origin of the sign of that second-order term. For practical applications of the theory to molecules containing heavy atoms,[2,3] the sign change had already been implemented in the computer programs in order to obtain a term which is repulsive and thus corrects for the overshooting of the Hamiltonian employing only the free-particle Foldy-Wouthuysen transformation. The formulas given[2,3] were, however, in error and should be corrected according to Eq. (16) in this Brief Report.

The first step in Douglas and Kroll's series of transformations consists of a free-particle Foldy-Wouthuysen transformation of the Dirac Hamiltonian in momentum space

$$H_D^{\text{ext}}=\boldsymbol{\alpha}\cdot\mathbf{p}+\beta m+V_{\text{ext}} \tag{1}$$

with

$$V_{\text{ext}}\Phi(\mathbf{p})=\int d^3p'\,V_{\text{ext}}(\mathbf{p},\mathbf{p}')\Phi(\mathbf{p}') \ . \tag{2}$$

The free-particle Foldy-Wouthuysen transformation with the unitary operator

$$U_0=A(1+\beta R),\quad U_0^{-1}=(R\beta+1)A \ , \tag{3}$$

where

$$A=\left[\frac{E_p+m}{2E_p}\right]^{1/2},\quad R=\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{E_p+m},\quad E_p=(\mathbf{p}^2+m^2)^{1/2}, \tag{4}$$

leads to

$$U_0H_D^{\text{ext}}U_0^{-1}=\beta E_p+\mathcal{E}_1+\mathcal{O}_1=H_1 \ . \tag{5}$$

$\mathcal{E}_1$ and $\mathcal{O}_1$ are, respectively, the even and odd operators of first order in the external potential. They are given by

$$\mathcal{E}_1\equiv A(V_{\text{ext}}+RV_{\text{ext}}R)A \ ,\quad \mathcal{O}_1\equiv\beta A(RV_{\text{ext}}-V_{\text{ext}}R)A \ , \tag{6}$$

where it has to be kept in mind that V_{ext} is an integral operator.

In order to remove the odd term, Douglas and Kroll noticed that the operator

$$U_1=(1+W_1^2)^{1/2}+W_1 \tag{7}$$

is unitary if W_1 is anti-Hermitian. Performing the transformation through U_1 and expanding the square root in powers of W_1 leads to

$$\begin{aligned}U_1H_1U_1^{-1}=&\beta E_p-[\beta E_p,W_1]+\mathcal{E}_1+\mathcal{O}_1\\&+\tfrac{1}{2}\beta E_pW_1^2+\tfrac{1}{2}W_1^2\beta E_p-W_1\beta E_pW_1\\&+[W_1,\mathcal{O}_1]+[W_1,\mathcal{E}_1]+\cdots\ ,\end{aligned} \tag{8}$$

where the centered dots denote terms in higher than second order of W_1. From this equation it is seen that $\mathcal{O}_1$

disappears if the condition

$$[\beta E_p, W_1] = \mathcal{O}_1 \tag{9}$$

or, equivalently,

$$W_1 E_p + E_p W_1 = \beta \mathcal{O}_1 \tag{10}$$

is imposed. In order to fulfill (10), it is sufficient to choose W_1 as an odd operator. Remembering now that $\mathcal{O}_1$ is an integral operator, the kernel of W_1 is given by

$$W_1(\mathbf{p},\mathbf{p}') = \beta \frac{\mathcal{O}_1(\mathbf{p},\mathbf{p}')}{E_{p'} + E_p} , \tag{11}$$

or, more explicitly, by

$$\begin{aligned} W_1(\mathbf{p},\mathbf{p}') &= A(R - R')A' \frac{V_{\text{ext}}(\mathbf{p},\mathbf{p}')}{E_{p'} + E_p} \\ &= \left[\frac{\boldsymbol{\alpha}\cdot\mathbf{p}}{\sqrt{2E_p(E_p+m)}} \left[\frac{E_{p'}+m}{2E_{p'}} \right]^{1/2} - \frac{\boldsymbol{\alpha}\cdot\mathbf{p}'}{\sqrt{2E_{p'}(E_{p'}+m)}} \left[\frac{E_p+m}{2E_p} \right]^{1/2} \right] \\ &\quad \times \frac{V_{\text{ext}}(p,p')}{E_{p'}+E_p} . \end{aligned} \tag{12}$$

Obviously, W_1 is of order V_{ext} and anti-Hermitian, as desired.

The remaining odd terms in the transformed Hamiltonian (8) are of order V_{ext}^2 or higher. Douglas and Kroll state that these terms can be removed by successive transformations of the same kind, where the operators U_n are given by

$$U_n = (1 + W_n^2)^{1/2} + W_n \tag{13}$$

and W_n is anti-Hermitian and of order V_{ext}^n. A transformation with the unitary operator U_n does not change the even terms up to and including order V_{ext}^n. So, with this procedure it is possible to decouple the upper and lower components of a Dirac spinor to any desired order of the external potential.

The transformed Dirac Hamiltonian correct to second order in the external potential is given by

$$\mathcal{H}_D^{\text{ext}} \equiv \beta E_p + \mathcal{E}_1 + \beta(W_1 E_p W_1 + \tfrac{1}{2}\{W_1^2, E_p\}) + [W_1, \mathcal{O}_1] , \tag{14}$$

where all terms of third and higher order have been neglected. The term $[W_1, \mathcal{O}_1]$, which is an even term of second order in the external potential, can be cast into another form using (9)

$$\begin{aligned} [W_1, \mathcal{O}_1] &= W_1[\beta E_p, W_1] - [\beta E_p, W_1]W_1 \\ &= -\beta(2W_1 E_p W_1 + E_p W_1^2 + W_1^2 E_p) . \end{aligned} \tag{15}$$

$\mathcal{H}_D^{\text{ext}}$ may now be written as

$$\mathcal{H}_D^{\text{ext}} = \beta E_p + \mathcal{E}_1 - \beta(W_1 E_p W_1 + \tfrac{1}{2}\{W_1^2, E_p\}) , \tag{16}$$

where the sign of the third term is a minus, instead of the plus found in the final version of the paper by Douglas and Kroll. It has to be restated here that the second-order terms do not contribute to the fine-structure splitting and thus were not of practical interest in their work.

It should be noticed that the form employing the commutation relation (15),

$$\mathcal{H}_D^{\text{ext}} = \beta E_p + \mathcal{E}_1 + \tfrac{1}{2}[W_1, \mathcal{O}_1] , \tag{17}$$

is more advantageous for practical evaluation than Eq. (16) itself.

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[1] M. Douglas and N. M. Kroll, Ann. Phys. (N. Y.) **82**, 89 (1974).

[2] B. A. Hess, Phys. Rev. A **33**, 3742 (1986).

[3] B. A. Hess and P. Chandra, Phys. Scr. **36**, 412 (1987).