Relativistic Electric and Magnetic Property Operators for Two-Component Transformed Hamiltonians

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ABSTRACT: A general procedure is presented for the derivation of property operators for electric and magnetic perturbations for Hamiltonians derived from the Dirac Hamiltonian by a partially block-diagonalizing unitary transformation. The procedure involves a regularized expansion in powers of $\mathbf{p}^2/m^2c^2$. Property operators are expressed in terms of the solid spherical harmonics. Expressions for the free-particle Foldy–Wouthuysen, Douglas–Kroll, and Barysz–Sadlej–Snijders transformations are compared with the well-known Pauli results. Explicit examples of a constant electric field and a constant magnetic field are given. © 2000 John Wiley & Sons, Inc. Int J Quantum Chem 78: 412–421, 2000

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Introduction

The development and implementation of the Douglas–Kroll transformation of the Dirac Hamiltonian by Hess and coworkers [1] into a one-component, one-electron formalism has enabled relativistic effects to be incorporated into standard quantum chemistry codes by a modification of the one-electron integrals. This approach is becoming increasingly widespread [2–4], and as a consequence there is interest in properties other than the energy, which arise from an external electric or magnetic field. The transformation of the Dirac Hamiltonian into an approximate block-diagonal form involves the so-called picture change of operators. This has been investigated and analyzed for electric perturbations by Sadlej et al. [5–7]. For magnetic perturbations some developments have been made by Fukui et al. [8, 9], but in the end only the Pauli correction to the magnetic perturbation was incorporated.

The apparent difficulty in applying the Douglas–Kroll transformation to operators other than the Coulomb potential led to the development of the point-charge model of the nuclear quadrupole moment by Pernpointner et al. [10] and Kellö and Sadlej [11]. To the author's knowledge, no expressions have been presented for property operators even within the free-particle Foldy–Wouthuysen transformation, let alone the Douglas–Kroll transformation, or the more recent series of transforma-

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tions proposed by Barysz et al. [12]. It is the object of this article to present a procedure for deriving property operators for these transformations.

General Considerations

We start with the Dirac Hamiltonian with rest mass subtracted,

$$\hat{\mathcal{H}}_D = c\boldsymbol{\alpha}\cdot\mathbf{p} + (\beta - 1)mc^2 + V, \tag{1}$$

which is represented in two-component form by

$$\hat{\mathcal{H}}_D = \begin{pmatrix} V & c\boldsymbol{\sigma}\cdot\mathbf{p} \\ c\boldsymbol{\sigma}\cdot\mathbf{p} & V - 2mc^2 \end{pmatrix}. \tag{2}$$

This Hamiltonian can in principle be block-diagonalized by a unitary transformation,

$$\hat{\mathcal{H}}^{\text{trans}} = \hat{\mathcal{U}}\hat{\mathcal{H}}_D\hat{\mathcal{U}}^{-1} = \begin{pmatrix} \hat{\mathcal{H}}_+ & 0 \\ 0 & \hat{\mathcal{H}}_- \end{pmatrix}. \tag{3}$$

In practice it is only possible to block-diagonalize to a certain order in some chosen parameter. The free-particle Foldy–Wouthuysen (FPFW) transformation, which performs the block-diagonalization exactly for a constant potential, is

$$\hat{\mathcal{U}}^{\text{FPFW}} = \beta\hat{\mathcal{A}}(\mathbf{I} + \hat{\mathcal{R}}), \tag{4}$$

where

$$\hat{\mathcal{A}} = \left(\frac{e_p + 1}{2e_p}\right)^{1/2}, \qquad \hat{\mathcal{R}} = \frac{1}{mc(e_p + 1)}\boldsymbol{\alpha}\cdot\mathbf{p}, \tag{5}$$

and e_p is the reduced free-particle energy,

$$e_p = \sqrt{1 + \mathbf{p}^2/m^2c^2}. \tag{6}$$

The transformed Hamiltonian is

$$\hat{\mathcal{H}}^{\text{FPFW}} = \beta mc^2(e_p - 1) + \hat{\mathcal{A}}\big(V + \hat{\mathcal{R}}V\hat{\mathcal{R}} + \beta[\hat{\mathcal{R}}, V]\big)\hat{\mathcal{A}}. \tag{7}$$

Defining the operator

$$\hat{\mathcal{Q}} = \big[2e_p(1 + e_p)\big]^{-1/2}, \tag{8}$$

the positive-energy block of the Hamiltonian can be written

$$\hat{H}_+^{\text{FPFW}} = mc^2(e_p - 1) + \hat{\mathcal{A}}V\hat{\mathcal{A}} + \frac{1}{m^2c^2}\hat{\mathcal{Q}}\boldsymbol{\sigma}\cdot\mathbf{p}V\boldsymbol{\sigma}\cdot\mathbf{p}\hat{\mathcal{Q}}. \tag{9}$$

The Pauli Hamiltonian is derived from a block-diagonalization of the Dirac Hamiltonian correct to order 2 in $\mathbf{p}/mc$,

$$\hat{\mathcal{U}}^{\text{Pauli}} = e^{\beta\boldsymbol{\alpha}\cdot\mathbf{p}/2mc}, \tag{10}$$

and for the purposes of this article we write the Hamiltonian as

$$\hat{\mathcal{H}}^{\text{Pauli}} = T + V - \frac{\mathbf{p}^4}{8m^3c^2} + \frac{\hbar^2}{8m^2c^2}(\nabla^2 V) + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\nabla V)\times\mathbf{p}. \tag{11}$$

The Douglas–Kroll (DK) transformation is normally applied after the FPFW transformation. One expression for the transformation is

$$\hat{\mathcal{U}}^{\text{DK}} = \big(1 + \hat{\mathcal{W}}^2\big)^{1/2} + \hat{\mathcal{W}}, \tag{12}$$

where $\hat{\mathcal{W}}$ is an off-diagonal operator. The square root is expanded to second order and the first-order term is eliminated according to

$$\hat{\mathcal{O}} + \big[\hat{\mathcal{W}}, \beta mc^2 e_p\big] = 0, \tag{13}$$

where

$$\hat{\mathcal{O}} = \beta\hat{\mathcal{A}}\big[V, \hat{\mathcal{R}}\big]\hat{\mathcal{A}}. \tag{14}$$

$\hat{\mathcal{W}}$ may be expressed as an integral operator in momentum space with kernel

$$\hat{\mathcal{W}}(\mathbf{p},\mathbf{p}') = \hat{\mathcal{A}}\tilde{V}(\mathbf{p},\mathbf{p}')\hat{\mathcal{R}}'\hat{\mathcal{A}}' - \hat{\mathcal{A}}\hat{\mathcal{R}}\tilde{V}(\mathbf{p},\mathbf{p}')\hat{\mathcal{A}}', \tag{15}$$

where the potential energy kernel is

$$\tilde{V}(\mathbf{p},\mathbf{p}') = \frac{V(\mathbf{p},\mathbf{p}')}{mc^2(e_p + e'_p)}. \tag{16}$$

It should be noted that the expansion of the square root to second order gives the same result as an exponential ansatz for $\hat{\mathcal{U}}$ in terms of $\hat{\mathcal{W}}$. The lowest-order Barysz–Sadlej–Snijders (BSS) transformation [12] (also applied after the FPFW transformation) can be written

$$\hat{\mathcal{U}}^{\text{BSS}} = \mathbf{I} - \frac{1}{2mc^2}\hat{\mathcal{O}}. \tag{17}$$

The corresponding Hamiltonians, correct to lowest order, are

$$\hat{\mathcal{H}}^{\text{DK}} = \beta mc^2(e_p - 1) + \hat{\mathcal{A}}\big(V + \hat{\mathcal{R}}V\hat{\mathcal{R}}\big)\hat{\mathcal{A}} - \beta mc^2\big(\hat{\mathcal{W}}_1 e_p\hat{\mathcal{W}}_1 + \tfrac{1}{2}\big[\hat{\mathcal{W}}_1^2, e_p\big]_+\big) \tag{18}$$

$$\hat{\mathcal{H}}^{\text{BSS}} = \beta mc^2(e_p - 1) + \hat{\mathcal{A}}\big(V + \hat{\mathcal{R}}V\hat{\mathcal{R}}\big)\hat{\mathcal{A}} - \frac{1}{2mc^2}\hat{\mathcal{A}}\big[V, \hat{\mathcal{R}}\big]\hat{\mathcal{A}}^2\big[V, \hat{\mathcal{R}}\big]\hat{\mathcal{A}}. \tag{19}$$

These two Hamiltonians can both be shown to be correct to $\mathcal{O}(c^{-4})$ in the expansion of the Dirac equation, and both can be used variationally. It should be further noted that the FPFW transformation is gauge-invariant (i.e., invariant to the addition of a constant to the potential) and hence all subsequent unitary transformations will be gauge-invariant.

In the Dirac equation an external electric field may be introduced by simply adding the potential due to the field, W, to the potential V. The operators for the potential have exactly the same form as the nonrelativistic operators. The transformed perturbation may be written

$$W^{\text{trans}} = \hat{\mathcal{U}} W \hat{\mathcal{U}}^{-1} = W + [\hat{\mathcal{U}}, W]\hat{\mathcal{U}}^{-1}. \tag{20}$$

The first term in this expression is essentially the nonrelativistic operator; the second term represents the picture change due to the transformation, or alternatively the relativistic correction to the operator. We will examine specific operators and procedures for evaluating the commutators below. Because the potential in the above transformation was a general potential, the behavior of the property operators under the transformations will be the same as for the Coulomb potential: the operator will be correct to second order in the property and correct to $\mathcal{O}(c^{-4})$ for the DK and BSS transformations. Note that the transformation $\hat{\mathcal{U}}$ will also in general be field-dependent, and in particular in any transformation subsequent to the FPFW transformation. In an applied field the off-diagonal operator $\hat{\mathcal{O}}$ from the FPFW transformation becomes

$$\hat{\mathcal{O}}^{W} = \beta\hat{\mathcal{A}}[V + W, \hat{\mathcal{R}}]\hat{\mathcal{A}}, \tag{21}$$

and the DK and BSS transformations will reflect this. Practically, it is simply a matter of substituting $V+W$ for V in the transformed Hamiltonian. The DK and BSS Hamiltonians will then contain terms quadratic in the applied field.

Magnetic perturbations are introduced via the vector potential, and we rewrite the Dirac equation with a vector potential,

$$\hat{\mathcal{H}}_D = c\boldsymbol{\alpha}\cdot(\mathbf{p} + e\mathbf{A}) + (\beta - 1)mc^2 + V. \tag{22}$$

The vector potential appears on the off-diagonal, and therefore must be included in any decoupling procedure. The FW transformation in $\mathbf{p}/mc$ produces integer powers of the momentum, and it is straightforward to substitute $\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})$ for $\mathbf{p}$ in the resulting Hamiltonian. The field-dependent Pauli Hamiltonian is [13–15]

$$\begin{aligned}
\hat{\mathcal{H}}^{\text{Pauli}} &= \frac{1}{2m}\big[\boldsymbol{\sigma}\cdot(\mathbf{p}\cdot e\mathbf{A})\big]^2 - \frac{1}{8m^3c^2}\big[\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})\big]^4 \\
&\quad + V - \frac{1}{8m^2c^2}\big[\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A}), [\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A}), V]\big] \\
&= \frac{\mathbf{p}^2}{2m} + \frac{e}{m}\mathbf{A}\cdot\mathbf{p} + \frac{e^2\mathbf{A}^2}{2m} + \frac{e\hbar}{2m}\boldsymbol{\sigma}\cdot\mathbf{B} \\
&\quad - \frac{1}{8m^3c^2}\big(\mathbf{p}^4 + e^2(\mathbf{p}^2\mathbf{A}^2 + \mathbf{A}^2\mathbf{p}^2) + e^4\mathbf{A}^4\big) \\
&\quad - \frac{e}{4m^3c^2}\big[\mathbf{A}\cdot\mathbf{p}(\mathbf{p}^2 + e^2\mathbf{A}^2) \\
&\qquad + (\mathbf{p}^2 + e^2\mathbf{A}^2)\mathbf{A}\cdot\mathbf{p}\big] \\
&\quad - \frac{e^2}{2m^3c^2}(\mathbf{A}\cdot\mathbf{p})^2 \\
&\quad - \frac{e\hbar}{8m^3c^2}\big[\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{p}^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2\mathbf{A}^2) \\
&\qquad + (p^2 + 2e\mathbf{A}\cdot\mathbf{p} + e^2\mathbf{A}^2)\boldsymbol{\sigma}\cdot\mathbf{B}\big] \\
&\quad - \frac{e^2\hbar^2}{8m^3c^2}\mathbf{B}^2 + V + \frac{\hbar^2}{8m^2c^2}(\nabla^2 V) \\
&\quad - \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})\times(\nabla V).
\end{aligned} \tag{23}$$

For a free particle in a magnetic field it is possible to define an exact block-diagonalizing transformation with the same substitution [9, 16]. We obtain a new two-component energy operator to replace e_p in all the expressions above,

$$\epsilon_p = \sqrt{\mathbf{I} + \big(\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})\big)^2/m^2c^2}. \tag{24}$$

With this operator we can define new operators $\hat{\mathcal{A}}$ and $\hat{\mathcal{R}}$ by substituting ϵ_p for e_p and $(\mathbf{p}+e\mathbf{A})$ for $\mathbf{p}$. The positive-energy block of the new transformed Hamiltonian is

$$\begin{aligned}
\hat{\mathcal{H}}^{\text{FPFW},\,m} &= mc^2(\epsilon_p - I) + \sqrt{\frac{\epsilon_p + 1}{2\epsilon_p}} \\
&\quad \times \left(V\mathbf{I} + \frac{\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})}{mc(\epsilon_p+1)}V\frac{\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})}{mc(\epsilon_p+1)}\right) \\
&\quad \times \sqrt{\frac{\epsilon_p + 1}{2\epsilon_p}}.
\end{aligned} \tag{25}$$

The Douglas–Kroll and Barysz–Sadlej–Snijders transformations may be defined by the same substitutions also, but will not be explicitly given here.

We are thus left with a perturbation-dependent Hamiltonian, which would necessitate the use of finite-field methods. For magnetic fields that represent a small perturbation (which is the case in most applications) it is sufficient to extract only the linear term, for which procedures are developed in the next section. For nonlinear terms it is straightforward to follow the same procedure.

Expansions of Momentum-Dependent Operators

The principal difficulty in the implementation of transformations based on the FPFW transformation is the presence of operators involving complicated functions of the momentum. The meaning of these operators must be defined in terms of an infinite expansion in integer powers of the momentum, or in momentum space where they are simply algebraic functions. The problem with the expansion is that it is not convergent for $p > mc$, but provided we do not truncate the expansion, we may make transformations on the series outside its radius of convergence as a representation of the operator and re-sum the series in the final result. It is this approach that we will use to obtain definitions of the property operators.

First, we obtain expressions for a general electric perturbation operator under a general transformation. The basic variable with which we have to deal is $\mathbf{p}^2/m^2c^2$, which we will denote x. We may write the commutator of an operator W with powers of x as

$$\begin{aligned}[x^n, W] &= n[x, W]x^{n-1} + \binom{n}{2}[x, [x, W]]x^{n-2} + \cdots \\ &= \sum_{k=1}^{n}\binom{n}{k}[x, W]^{(k)}x^{n-k} \\ &= \sum_{k=1}^{n}[x, W]^{(k)}\frac{1}{k!}\left(\frac{d}{dx}\right)^k x^n, \end{aligned} \tag{26}$$

where we have defined the kth order multiple commutator

$$[x, W]^{(k)} = [x, [x, \ldots [x, W]]] \tag{27}$$

with k occurrences of x. By extension, the commutator of any function of x can be written

$$[f(x), W] = \sum_{k=1}^{\infty}[x, W]^{(k)}\frac{1}{k!}\left(\frac{d}{dx}\right)^k f(x). \tag{28}$$

The task of defining the perturbation operator then reduces to that of evaluating the multiple commutators and the derivatives of the operators, with the exception of the term involving $\boldsymbol{\sigma}\cdot\mathbf{p}$ which must be evaluated explicitly.

A few comments are appropriate here. Provided the derivatives are evaluated exactly, and not expanded in a series and truncated, the regularization of the operators will be retained, and there will be no problems with divergences. Furthermore, the sum over the multiple commutators is in powers of $x = (\mathbf{p}/mc)^2$, which provides an expansion of the relativistic correction in powers of $1/c^2$.

A similar procedure may be used for the magnetic perturbations. We wish to expand the field-dependent operators in powers of the vector potential. The expansion involves even powers of the operator $\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})$, whose square may be written

$$\big(\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})\big)^2 = \mathbf{p}^2 + e(2\mathbf{A}\cdot\mathbf{p} + \hbar\boldsymbol{\sigma}\cdot\mathbf{B}) + e^2\mathbf{A}^2, \tag{29}$$

where we have made use of the Dirac relation $\boldsymbol{\sigma}\cdot\mathbf{u}\boldsymbol{\sigma}\cdot\mathbf{v} = \mathbf{u}\cdot\mathbf{v} + i\boldsymbol{\sigma}\cdot\mathbf{u}\times\mathbf{v}$ and the Coulomb gauge in which $\nabla\cdot\mathbf{A} = 0$. $\mathbf{B}$ is the magnetic field; $\mathbf{B} = \nabla\times\mathbf{A}$. We will be concerned here principally with the term linear in $\mathbf{A}$, but it is straightforward to extend to higher order terms. The expansion of even powers of $\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})$ gives

$$\begin{aligned}&\big(\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})\big)^{2n} \\ &\quad= \mathbf{p}^{2n} + e\sum_{k=1}^{n}\mathbf{p}^{2k-2}(2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B})\mathbf{p}^{2n-2k} + \cdots \\ &\quad= \mathbf{p}^{2n} + e\sum_{k=1}^{n}\binom{n}{k}\big[\mathbf{p}^2, (2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B})\big]^{(k-1)} \\ &\qquad\times\mathbf{p}^{2n-2k} + \cdots \\ &\quad= \mathbf{p}^{2n} + e\sum_{k=1}^{n}\big[\mathbf{p}^2, (2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B})\big]^{(k-1)} \\ &\qquad\times\frac{1}{k!}\left(\frac{d}{d\mathbf{p}^2}\right)^k\mathbf{p}^{2n} + \cdots, \end{aligned} \tag{30}$$

where the 0th-order commutator is defined to be $[x, y]^{(0)} = y$. The powers of $(\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A}))^2$ must be divided by m^2c^2, and writing $y = (\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A}))^2/m^2c^2$ we have

$$\begin{aligned}f(y) = f(x) + \frac{e}{m^2c^2}\sum_{k=1}^{\infty}\big[x, (2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B})\big]^{(k-1)} \\ \times\frac{1}{k!}\left(\frac{d}{dx}\right)^k f(x) + \cdots. \end{aligned} \tag{31}$$

This expression is very similar to the one for the electric perturbations.

The task of defining the operators therefore reduces to differentiating various functions of $\mathbf{p}^2$ and evaluating the multiple commutators over the gradient operators, the first two of which can be written in general form as

$$\begin{aligned}[\nabla^2, f] &= (\nabla^2 f) + 2(\nabla f)\cdot\nabla, \\ [\nabla^2, [\nabla^2, f]] &= (\nabla^4 f) + 4\big(\nabla(\nabla^2 f)\big)\cdot\nabla \\ &\quad + 4\big(\nabla(\nabla f)\cdot\nabla\big)\cdot\nabla. \end{aligned} \tag{32}$$

In this section we have commuted the property operators to the left. We could equally well have commuted them to the right—and in fact doing both will provide symmetric expressions for the final operators, rather than asymmetric expressions.

Property Operators

The molecular properties of primary interest are those which are a response to the application of an external electric or magnetic field, or those which arise from nuclear electric or magnetic moments. For both classes, the property operators can be expressed in terms of the regular or irregular solid spherical harmonics (SSHs) [17],

$$S^{\mathrm{R}}_{\ell m}(\mathbf{r}) = r^{\ell} C_{\ell m}(\theta, \phi), \qquad S^{\mathrm{I}}_{\ell m}(\mathbf{r}) = r^{-\ell-1} C_{\ell m}(\theta, \phi), \tag{33}$$

where the $C_{\ell m}$ are spherical tensors related to the usual spherical harmonics by $\sqrt{4\pi}\, Y_{\ell m} = \sqrt{2\ell+1}\, C_{\ell m}$. From this point on, we will be making extensive use of definitions from Brink and Satchler [17] which will not be further referenced. Here the properties of these functions will be reviewed in the context of the application to property operators.

External electric and magnetic fields transform as the regular SSHs and nuclear fields for a point nucleus as the irregular SSHs. These functions have special properties from which it is relatively easy to derive the commutators of the previous section. From the lowest order commutator in Eq. (32) there are two terms. The Laplacian of the SSHs is

$$\nabla^2 S^{\mathrm{R}}_{\ell m} = 0; \qquad \nabla^2 S^{\mathrm{I}}_{\ell m} = -4\pi\, \delta_{\ell m}(\mathbf{r}), \tag{34}$$

where the spherical tensor delta function is defined by

$$\int d^3\mathbf{r}\, \delta_{\ell m}(\mathbf{r}) S^{\mathrm{R}}_{\ell' m'}(\mathbf{r}) = \delta_{\ell,\ell'} \delta_{m,m'}. \tag{35}$$

The other derivative term is

$$\begin{aligned} \nabla S^{\mathrm{R}}_{\ell m} \cdot \nabla &= \sqrt{\ell(2\ell-1)}\, T_{\ell m}\big(\mathbf{S}^{\mathrm{R}}_{\ell-1}, \nabla\big), \\ \nabla S^{\mathrm{I}}_{\ell m} \cdot \nabla &= \sqrt{(\ell+1)(2\ell+3)}\, T_{\ell m}\big(\mathbf{S}^{\mathrm{I}}_{\ell+1}, \nabla\big), \end{aligned} \tag{36}$$

where $\mathbf{T}_\ell$ is a solid spherical tensor formed by coupling the angular parts of its two arguments. The effect of the derivative operator is to replace one power of $\mathbf{r}$ with one power of ∇ in the original SSH. The result is the coupling of a SSH of lower rank by one to ∇ in the regular case and the coupling of a SSH of higher rank by one to ∇ in the irregular case. The results for the commutator are

$$\big[\nabla^2, \mathbf{S}^{\mathrm{R}}_{\ell}\big] = \sqrt{\ell(2\ell-1)}\, \mathbf{T}_\ell\big(\mathbf{S}^{\mathrm{R}}_{\ell-1}, \nabla\big), \tag{37}$$

$$\big[\nabla^2, \mathbf{S}^{\mathrm{I}}_{\ell}\big] = -4\pi\, \boldsymbol{\delta}_\ell(\mathbf{r}) + \sqrt{(\ell+1)(2\ell+3)}\, \mathbf{T}_\ell\big(\mathbf{S}^{\mathrm{I}}_{\ell+1}, \nabla\big). \tag{38}$$

From the next order commutator in Eq. (32), the first and second terms are zero for the regular SSHs. In the third term, each application of $\nabla \cdot \nabla$ replaces one occurrence of $\mathbf{r}$ with an occurrence of ∇; hence the operator is progressively transformed from one in powers of $\mathbf{r}$ to one in powers of $\mathbf{p}$. The transformation properties of the spherical tensor are unchanged in the process, and the result is

$$\begin{aligned} \big[\nabla^2, \big[\nabla^2, \mathbf{S}^{\mathrm{R}}_{\ell}\big]\big] &= 4\sqrt{\ell(\ell-1)(2\ell-1)(2\ell-3)} \\ &\quad \times \mathbf{T}_\ell\big(\mathbf{T}_{\ell-1}\big(\mathbf{S}^{\mathrm{R}}_{\ell-2}, \nabla\big), \nabla\big). \end{aligned} \tag{39}$$

For the irregular SSHs, application of ∇^2 to the spherical tensor delta function produces another delta function,

$$\delta^n_{\ell,m}(\mathbf{r}) = \frac{(n+\ell)!(2\ell+1)!}{n!\ell!(2n+2\ell+1)!} \nabla^{2n} \delta_{\ell m}(\mathbf{r}), \tag{40}$$

with the property

$$\int d^3\mathbf{r}\, \delta^n_{\ell m}(\mathbf{r}) r^{2n'} S^{\mathrm{R}}_{\ell' m'}(\mathbf{r}) = \delta_{n,n'} \delta_{\ell,\ell'} \delta_{m,m'}. \tag{41}$$

The second term is interpreted by taking the Laplacian of the $\nabla S^{\mathrm{I}}_{\ell m} \cdot \nabla$ term, which produces a delta function of rank $\ell+1$; the third term is analogous to the regular case. The final result is

$$\begin{aligned} \big[\nabla^2, \big[\nabla^2, \mathbf{S}^{\mathrm{I}}_{\ell}\big]\big] &= -8\pi(2\ell+3)\delta^1_\ell(\mathbf{r}) \\ &\quad - 16\pi\sqrt{(\ell+1)(2\ell+3)}\, \mathbf{T}_\ell(\delta_{\ell+1}, \nabla) \\ &\quad + 4\sqrt{(\ell+1)(\ell+2)(2\ell+3)(2\ell+5)} \\ &\quad \times \mathbf{T}_\ell\big(\mathbf{T}_{\ell+1}\big(\mathbf{S}^{\mathrm{I}}_{\ell+2}, \nabla\big), \nabla\big). \end{aligned} \tag{42}$$

Continuation of this series follows the obvious course. For the regular SSHs the multiple commutator vanishes for $k > \ell$; for the irregular SSHs the multiple commutator does not vanish, and the powers of the gradient operator ensure that the integrals over the basis functions do not vanish, despite the increasing angular momentum of the SSHs and the delta functions.

The contributions to the Hamiltonian from the property operators must be scalar quantities. For electric perturbations these can easily be expressed in terms of a scalar product of a spherical tensor of field strengths $\mathbf{F}^{\mathrm{E}}_k$ and a SSH,

$$W^{\mathrm{C}}_k = \mathbf{F}^{\mathrm{E,C}}_k \cdot \mathbf{S}^{\mathrm{C}}_k, \tag{43}$$

where C stands for R or I. For magnetic perturbations, the vector potential is usually expressed as a vector product, which can be written in terms of spherical tensors as

$$\mathbf{a} \times \mathbf{b} = -\sqrt{2}i\, \mathbf{T}_1(\mathbf{a}, \mathbf{b}). \tag{44}$$

This expression covers the case of a constant magnetic field and a nuclear magnetic moment. In the more general case we simply use the rank 1 tensor product, and write

$$\mathbf{A}_k^{\mathrm{C}} = -\sqrt{2}i\,\mathbf{T}_1\big(\mathbf{F}_k^{\mathrm{M,C}}, \mathbf{S}_k^{\mathrm{C}}\big), \tag{45}$$

where $\mathbf{F}_k^{\mathrm{M,C}}$ is the magnetic field strength tensor. The contribution to the Hamiltonian comes from the scalar product of $\mathbf{A}$ with $\boldsymbol{\sigma}$ or $\boldsymbol{\alpha}$,

$$\boldsymbol{\sigma}\cdot\mathbf{A} = -\sqrt{2}i\boldsymbol{\sigma}\cdot\mathbf{T}_1\big(\mathbf{F}_k^{\mathrm{M,C}}, \mathbf{S}_k^{\mathrm{C}}\big). \tag{46}$$

Since the commutator relations above do not change the tensorial properties of the operators, and since the gradient operator only operates on the SSHs, the commutators of the powers of ∇^2 with the electric and magnetic perturbations are easily derived by simply substituting the appropriate commutator expression for the SSH in the property operator.

Apart from the commutator expressions, there are several operators which arise in the relativistic corrections to electric and magnetic perturbations. From the electric perturbations we have the operator

$$\boldsymbol{\sigma}\cdot\mathbf{p}W\boldsymbol{\sigma}\cdot\mathbf{p} = -\hbar^2(\nabla W)\cdot\nabla + \hbar\boldsymbol{\sigma}\cdot(\nabla W)\times\mathbf{p} + W\mathbf{p}^2. \tag{47}$$

The first of these is of the type dealt with above. The second is a spin-orbit operator which we rearrange to $-(\nabla W)\cdot\boldsymbol{\sigma}\times\mathbf{p}$. Writing the vector product in terms of a spherical tensor of rank 1, this operator can be written

$$\begin{aligned}\boldsymbol{\sigma}\cdot\big(\nabla W_k^{\mathrm{R}}\big)\times\mathbf{p} &= i\sqrt{(2k-1)(2k)}\\ &\quad\times\mathbf{F}_k^{\mathrm{E,R}}\cdot\mathbf{T}_k\big(\mathbf{S}_{k-1}^{\mathrm{R}}, \mathbf{T}_1(\boldsymbol{\sigma},\mathbf{p})\big),\\ \boldsymbol{\sigma}\cdot\big(\nabla W_k^{\mathrm{I}}\big)\times\mathbf{p} &= i\sqrt{(2k+2)(2k+3)}\\ &\quad\times\mathbf{F}_k^{\mathrm{E,I}}\cdot\mathbf{T}_k\big(\mathbf{S}_{k+1}^{\mathrm{I}}, \mathbf{T}_1(\boldsymbol{\sigma},\mathbf{p})\big).\end{aligned} \tag{48}$$

We see here that we are replacing one power of $\mathbf{r}$ with $\boldsymbol{\sigma}\times\mathbf{p}$. The third needs no further discussion at this point.

From the magnetic perturbations linear in the field we have the operators $\mathbf{A}\cdot\mathbf{p}$ and $\boldsymbol{\sigma}\cdot\mathbf{B} = \boldsymbol{\sigma}\cdot(\nabla\times\mathbf{A})$. For both of these we require the commutator with ∇^2 as given in general by Eq. (32). The Laplacian of $\mathbf{A}_k^{\mathrm{R}}$ is zero, and the Laplacian of $\mathbf{A}_k^{\mathrm{I}}$, the SSH, may be replaced by -4π times the spherical delta function of the same rank. The second term can be written as

$$(\nabla\mathbf{A}_k\cdot\mathbf{p})\cdot\nabla = \hbar\left[\frac{3(2k+1\pm2)(2k+1\pm3)}{10}\right]^{1/2} \times\mathbf{T}_2(\mathbf{S}_{k\pm1},\mathbf{F}_k)\cdot\mathbf{T}_2(\nabla,\nabla), \tag{49}$$

where the $+$ sign applies to the irregular and the $-$ sign to the regular SSH. This term is zero for a constant magnetic field. The magnetic field can be expressed in terms of the SSHs as

$$\begin{aligned}\mathbf{B}_k^{\mathrm{R}} &= \sqrt{(2k-1)(2k+2)}\,\mathbf{T}_1\big(\mathbf{F}_k, \mathbf{S}_{k-1}^{\mathrm{R}}\big),\\ \mathbf{B}_k^{\mathrm{I}} &= -\sqrt{(2k)(2k+3)}\,\mathbf{T}_1\big(\mathbf{F}_k, \mathbf{S}_{k+1}^{\mathrm{I}}\big).\end{aligned} \tag{50}$$

Evaluating the commutator of $\boldsymbol{\sigma}\cdot\mathbf{B}$ with the Laplacian yields the following results:

$$\nabla^2\boldsymbol{\sigma}\cdot\mathbf{B}_k^{\mathrm{I}} = (-1)^k 4\pi\left[\frac{3k(2k+3)}{k+1}\right]^{1/2} \times\boldsymbol{\delta}_{k+1}\cdot\mathbf{T}_{k+1}(\mathbf{F}_k,\boldsymbol{\sigma}), \tag{51}$$

$$\begin{aligned}\big(\nabla\boldsymbol{\sigma}\cdot\mathbf{B}_k^{\mathrm{I}}\big)\cdot\nabla &= (2k+3)\left[\frac{3k(k+2)(2k+5)}{5(k+1)}\right]^{1/2}\\ &\quad\times\mathbf{T}_2(\mathbf{S}_{k+2},\mathbf{F}_k)\cdot\mathbf{T}_2(\nabla,\boldsymbol{\sigma}),\\ \big(\nabla\boldsymbol{\sigma}\cdot\mathbf{B}_k^{\mathrm{R}}\big)\cdot\nabla &\\ &= -(2k-1)\left[\frac{3(k+1)(k-1)(2k-3)}{5k}\right]^{1/2}\\ &\quad\times\mathbf{T}_2(\mathbf{S}_{k-2},\mathbf{F}_k)\cdot\mathbf{T}_2(\nabla,\boldsymbol{\sigma}).\end{aligned} \tag{52}$$

These are, of course, not the only forms in which the operators may be expressed: one alternative is in terms of the scalar product $\mathbf{T}_{k\pm1}(\mathbf{S}_{k\pm2},\nabla)\cdot\mathbf{T}_{k\pm1}(\mathbf{F}_k,\boldsymbol{\sigma})$. Regardless of the particular form, the spherical tensor now differs from the original by 2 units of angular momentum. Again, for a constant magnetic field the commutator is zero.

Application to Various Transformations

We now come to apply the principles derived above to various transformations. We start with the Pauli approximation, for which expressions are already known. These are useful for comparison with the other approximations which must reduce to the Pauli approximation at the appropriate level of truncation. First, there is no scalar relativistic correction to the external field operators, because the Laplacian of the regular SSHs vanishes. There is however a spin-orbit correction, and for the nuclear fields there is both a scalar and a spin-orbit correction, which can be written

$$\begin{aligned}W_k^{\mathrm{Pauli,E,R}} &= \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\big(\nabla W_k^{\mathrm{E,R}}\big)\times\mathbf{p}\\ &= \frac{i\hbar}{4m^2c^2}\sqrt{(2k-1)(2k)}\\ &\quad\times\mathbf{F}_k^{\mathrm{E,R}}\cdot\mathbf{T}_k\big(\mathbf{S}_{k-1}^{\mathrm{R}},\mathbf{T}_1(\boldsymbol{\sigma},\mathbf{p})\big),\end{aligned} \tag{53}$$

$$\begin{aligned}W_k^{\mathrm{Pauli,E,I}} &= \frac{\hbar^2}{8m^2c^2}\big(\nabla^2 W_k^{\mathrm{E,I}}\big) + \frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\big(\nabla W_k^{\mathrm{E,I}}\big)\times\mathbf{p}\\ &= -\frac{\pi\hbar^2}{2m^2c^2}\mathbf{F}_k^{\mathrm{E,I}}\cdot\boldsymbol{\delta}_k\end{aligned}$$

$$+\frac{i\hbar}{4m^2c^2}\sqrt{(2k+2)(2k+3)}\times \mathbf{F}_k^{\mathrm{E,I}}\cdot \mathbf{T}_k\big(\mathbf{S}_{k+1}^{\mathrm{I}},\mathbf{T}_1(\boldsymbol{\sigma},\mathbf{p})\big). \quad (54)$$

For the simplest case of the dipole operator we obtain

$$W_1^{\mathrm{Pauli,E,R}} = e\mathbf{E}\cdot\left(\mathbf{r}+\frac{\hbar}{4m^2c^2}\boldsymbol{\sigma}\times\mathbf{p}\right). \quad (55)$$

The magnetic perturbations are easily deduced from Eq. (23). The terms linear in the vector potential yield

$$-\frac{e}{8m^3c^2}\big[(2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B})\mathbf{p}^2+\mathbf{p}^2(2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B})\big] - \frac{e\hbar}{4m^2c^2}\boldsymbol{\sigma}\cdot\mathbf{A}\times(\nabla V). \quad (56)$$

The first term is a kinetic relativistic correction and the second a correction due to the potential. For a constant magnetic field, $\mathbf{A}=\frac{1}{2}\mathbf{B}\times\mathbf{r}$, $\mathbf{p}^2$ commutes with the operators in parentheses, and the above expression reduces to

$$-\frac{e}{4m^3c^2}(\ell+\hbar\boldsymbol{\sigma})\cdot\mathbf{B}\mathbf{p}^2+\frac{e\hbar}{8m^2c^2}\mathbf{B}\times\mathbf{r}\cdot\boldsymbol{\sigma}\times(\nabla V). \quad (57)$$

For a nuclear magnetic moment $\mathbf{A}=\boldsymbol{\mu}\times\mathbf{r}/r^3$ and $\mathbf{B}=-\boldsymbol{\mu}/r^3+3\mathbf{r}(\boldsymbol{\mu}\cdot\mathbf{r})/r^5$. Then with some rearrangement we can write

$$2\mathbf{A}\cdot\mathbf{p}+\hbar\boldsymbol{\sigma}\cdot\mathbf{B}=\frac{2\boldsymbol{\mu}\cdot(\ell+\hbar\boldsymbol{\sigma})}{r^3}-\frac{3\hbar(\boldsymbol{\sigma}\times\mathbf{r})\cdot(\boldsymbol{\mu}\times\mathbf{r})}{r^5}, \quad (58)$$

which does not commute with $\mathbf{p}^2$. The resulting expression is more easily expressed in terms of the SSHs. However, in any implementation, there would be no need to evaluate the commutator, because $\mathbf{p}^2$ would be applied to the wave function, operating either to the right or the left.

For electric perturbations under the FPFW and subsequent transformations, the same principle applies in the implementation. It would not be necessary to evaluate any commutators, but simply to evaluate the matrix elements over the perturbation in the same way as the matrix elements over the potential. However, for the purposes of this paper, we wish to develop the formal theory of the electric perturbations and expand the perturbation operator in (regularized) powers of c^2. We will develop the expansion to $\mathcal{O}(c^{-4})$, which is the order to which the DK and BSS transformations are correct.

The FPFW transformation provides terms of two different orders in c^2, which must be combined in the final expression. Writing out the commutators with use of the Dirac relation we have

$$\begin{aligned}W^{\mathrm{FPFW}} &= \hat{\mathcal{A}}W\hat{\mathcal{A}}+\frac{1}{m^2c^2}\hat{\mathcal{Q}}\boldsymbol{\sigma}\cdot\mathbf{p}W\boldsymbol{\sigma}\cdot\mathbf{p}\hat{\mathcal{Q}}\\ &= W+\big[\hat{\mathcal{A}},W\big]\hat{\mathcal{A}}+\big[\hat{\mathcal{Q}},W\big]\frac{\mathbf{p}^2}{m^2c^2}\hat{\mathcal{Q}}\\ &\quad+\frac{1}{m^2c^2}(\mathbf{p}W)\cdot\mathbf{p}\hat{\mathcal{Q}}^2\\ &\quad+\frac{1}{m^2c^2}\big[\hat{\mathcal{Q}},(\mathbf{p}W)\cdot\mathbf{p}\big]\hat{\mathcal{Q}}\\ &\quad+\frac{\hbar}{m^2c^2}\boldsymbol{\sigma}\cdot(\nabla W)\times\mathbf{p}\hat{\mathcal{Q}}^2\\ &\quad+\frac{\hbar}{m^2c^2}\big[\hat{\mathcal{Q}},\boldsymbol{\sigma}\cdot(\nabla W)\times\mathbf{p}\big]\hat{\mathcal{Q}}. \end{aligned} \quad (59)$$

Expanding the commutators in the scalar terms and re-expressing $\mathbf{p}^2/m^2c^2$ in terms of e_p, we have

$$\begin{aligned}&\big[\hat{\mathcal{A}},W\big]\hat{\mathcal{A}}+\big[\hat{\mathcal{Q}},W\big]\frac{\mathbf{p}^2}{m^2c^2}\hat{\mathcal{Q}}\\ &\quad=-\frac{[\mathbf{p}^2,W]}{m^2c^2}\cdot\frac{1}{4e_p(1+e_p)}\\ &\qquad+\frac{[\mathbf{p}^2,[\mathbf{p}^2,W]]}{2m^4c^4}\cdot\frac{6e_p^2+4e_p+1}{16e_p^4(1+e_p)^2}+\cdots,\\ &\frac{1}{m^2c^2}(\mathbf{p}W)\cdot\mathbf{p}\hat{\mathcal{Q}}^2=\frac{(\mathbf{p}W)\cdot\mathbf{p}}{m^2c^2}\cdot\frac{1}{2e_p(1+e_p)},\\ &\frac{1}{m^2c^2}\big[\hat{\mathcal{Q}},(\mathbf{p}W)\cdot\mathbf{p}\big]\hat{\mathcal{Q}}\\ &\quad=-\frac{[\mathbf{p}^2,(\mathbf{p}W)\cdot\mathbf{p}]}{m^4c^4}\frac{2e_p+1}{8e_p^3(1+e_p)^2}+\cdots. \end{aligned} \quad (60)$$

The spin-orbit terms may be obtained by replacing $(\mathbf{p}W)\cdot\mathbf{p}$ with $\hbar\boldsymbol{\sigma}\cdot(\nabla W)\times\mathbf{p}$ in the last two expressions. Since $[\mathbf{p}^2,W]=(\mathbf{p}^2W)+2(\mathbf{p}W)\cdot\mathbf{p}$, the second expression cancels part of the first term in the first expression and similarly for the third expression. The final result, correct to $\mathcal{O}(c^{-4})$, is

$$\begin{aligned}W^{\mathrm{FPFW}} &= W+\frac{\hbar^2}{m^2c^2}(\nabla^2W)\frac{1}{4e_p(1+e_p)}\\ &\quad+\frac{\hbar}{m^2c^2}\boldsymbol{\sigma}\cdot(\nabla W)\times\mathbf{p}\frac{1}{2e_p(1+e_p)}\\ &\quad+\frac{\hbar^4}{m^4c^4}\big[\nabla^2,(\nabla^2W)\big]\frac{6e_p^2+4e_p+1}{32e_p^4(1+e_p)^2}\\ &\quad+\frac{\hbar^4}{m^4c^4}\big[\nabla^2,(\nabla W)\cdot\nabla\big]\frac{2e_p^2+2e_p+1}{16e_p^4(1+e_p)^2}\\ &\quad+\frac{\hbar^3}{m^4c^4}\big[\nabla^2,\boldsymbol{\sigma}\cdot(\nabla W)\times\mathbf{p}\big]\frac{2e_p+1}{8e_p^3(1+e_p)^2}. \end{aligned} \quad (61)$$

In the limit $e_p \to 1$, the lowest-order term is the same as the Pauli expression above, as it should be, and there is therefore no scalar term of $\mathcal{O}(c^{-2})$ for external electric fields, described by the regular SSHs. The cancellation which eliminated the $(\nabla W) \cdot \nabla$ term at $\mathcal{O}(c^{-2})$ is incomplete at $\mathcal{O}(c^{-4})$ and therefore one obtains two scalar terms, one of which will be zero for the regular SSHs. The second will reduce to an expression containing $(\nabla(\nabla W) \cdot \nabla) \cdot \nabla$. It should be noted that these are the pure kinetic corrections to the operator. The cross-terms involving the potential only appear with the DK or BSS transformation.

The magnetic terms from the FPFW transformation are derived from Eq. (25). The pure kinetic corrections come from ϵ_p, which we expand to $\mathcal{O}(c^{-4})$ to obtain

$$mc^2\epsilon_p = mc^2 e_p + eY\frac{1}{4me_p} + \left[\nabla^2, Y\right]\frac{e\hbar^2}{8m^3c^2e_p^3} + \left[\nabla^2, \left[\nabla^2, Y\right]\right]\frac{e\hbar^4}{16m^5c^4e_p^5} + \cdots, \quad (62)$$

where $Y = 2\mathbf{A} \cdot \mathbf{p} + \boldsymbol{\sigma} \cdot \mathbf{B}$. For a constant magnetic field all the commutators vanish, leaving only the first term in Y. If we expand e_p in powers of $\mathbf{p}^2/m^2c^2$ we obtain the kinetic correction to the Pauli operator, given above. For a nuclear magnetic field the series will not truncate, and the expressions given in the previous section for the irregular SSHs and their combinations must be used to obtain the operator to the desired order. The expression given here is not symmetric but is easily symmetrized in the expansion by halving each term and commuting Y to the right and to the left, instead of only commuting Y to the left.

To obtain the cross-terms between the magnetic field and the potential, the field-dependent FPFW potential terms are written in symmetric form as

$$\hat{\mathcal{A}}^Y V \hat{\mathcal{A}}^Y + \frac{1}{m^2c^2}\hat{\mathcal{Q}}^Y\bigg(\boldsymbol{\sigma} \cdot \mathbf{p} V \boldsymbol{\sigma} \cdot \mathbf{p} + e^2\boldsymbol{\sigma} \cdot \mathbf{A} V \boldsymbol{\sigma} \cdot \mathbf{A} + \frac{1}{2}e(VY + YV) + e\boldsymbol{\sigma} \cdot (\nabla V) \times \mathbf{A}\bigg)\hat{\mathcal{Q}}^Y, \quad (63)$$

where the superscripts indicate field-dependent operators. When expanding these operators, the field term Y is commuted to the left or the right, depending on where the primed operator is located. This yields a symmetric expression. The expansion up to $\mathcal{O}(c^{-4})$ for operators linear in the field is

$$\begin{aligned}
-\frac{e}{m^2c^2}\bigg(& Y\frac{1}{4e_p^2(1+e_p)}\hat{\mathcal{A}}V\hat{\mathcal{A}} + \hat{\mathcal{A}}V\hat{\mathcal{A}}\frac{1}{4e_p^2(1+e_p)}Y \\
&- \frac{[\mathbf{p}^2, Y]}{2m^2c^2}\frac{6e_p+5}{16e_p^4(1+e_p)^2}\hat{\mathcal{A}}V\hat{\mathcal{A}} \\
&- \hat{\mathcal{A}}V\hat{\mathcal{A}}\frac{6e_p+5}{16e_p^4(1+e_p)^2}\frac{[Y, \mathbf{p}^2]}{2m^2c^2} \\
&+ Y\frac{2e_p+1}{4e_p^2(1+e_p)}\hat{\mathcal{Q}}\frac{\boldsymbol{\sigma} \cdot \mathbf{p} V \boldsymbol{\sigma} \cdot \mathbf{p}}{m^2c^2}\hat{\mathcal{Q}} \\
&+ \hat{\mathcal{Q}}\frac{\boldsymbol{\sigma} \cdot \mathbf{p} V \boldsymbol{\sigma} \cdot \mathbf{p}}{m^2c^2}\hat{\mathcal{Q}}\frac{2e_p+1}{4e_p^2(1+e_p)}Y \\
&- \frac{[\mathbf{p}^2, Y]}{2m^2c^2}\frac{(6e_p+5)(2e_p+1)-2e_p}{16e_p^4(1+e_p)^2} \\
&\times \hat{\mathcal{Q}}\frac{\boldsymbol{\sigma} \cdot \mathbf{p} V \boldsymbol{\sigma} \cdot \mathbf{p}}{m^2c^2}\hat{\mathcal{Q}} \\
&- \hat{\mathcal{Q}}\frac{\boldsymbol{\sigma} \cdot \mathbf{p} V \boldsymbol{\sigma} \cdot \mathbf{p}}{m^2c^2}\hat{\mathcal{Q}}\frac{(6e_p+5)(2e_p+1)-2e_p}{16e_p^4(1+e_p)^2} \\
&\times \frac{[Y, \mathbf{p}^2]}{2m^2c^2} \\
&- \hat{\mathcal{Q}}\hbar\boldsymbol{\sigma} \cdot (\nabla V) \times \mathbf{A}\hat{\mathcal{Q}} - \frac{1}{2}\hat{\mathcal{Q}}(YV + VY)\hat{\mathcal{Q}}\bigg).
\end{aligned} \quad (64)$$

With the use of the relations $\hat{\mathcal{A}} = (1 + e_p)\hat{\mathcal{Q}}$ and $e_p^2 - 1 = \mathbf{p}^2/m^2c^2$, we rearrange terms on the first, fourth, fifth, and last lines to give

$$\begin{aligned}
& Y\frac{1}{4e_p^2(1+e_p)}\hat{\mathcal{A}}V\hat{\mathcal{A}} + Y\frac{2e_p+1}{4e_p^2(1+e_p)}\hat{\mathcal{Q}}\frac{\boldsymbol{\sigma} \cdot \mathbf{p} V \boldsymbol{\sigma} \cdot \mathbf{p}}{m^2c^2}\hat{\mathcal{Q}} \\
&\quad - \frac{1}{2}\hat{\mathcal{Q}}YV\hat{\mathcal{Q}} \\
&= Y\frac{1}{4e_p^2}\hat{\mathcal{Q}}[V, e_p]\hat{\mathcal{Q}} \\
&\quad + Y\frac{2e_p+1}{4e_p^2(1+e_p)}\hat{\mathcal{Q}}\frac{\boldsymbol{\sigma} \cdot \mathbf{p}[V, \boldsymbol{\sigma} \cdot \mathbf{p}]}{m^2c^2}\hat{\mathcal{Q}} \\
&\quad - \frac{1}{2}\left[\hat{\mathcal{Q}}, Y\right]V\hat{\mathcal{Q}}.
\end{aligned} \quad (65)$$

The terms which contributed to the final result at $\mathcal{O}(c^{-2})$ have cancelled, leaving commutators which contribute at $\mathcal{O}(c^{-4})$. Thus the lowest-order scalar relativistic correction vanishes, leaving as the lowest order term the spin-dependent operator

$$\frac{e\hbar}{m^2c^2}\hat{\mathcal{Q}}\boldsymbol{\sigma} \cdot (\nabla V) \times \mathbf{A}\hat{\mathcal{Q}}, \quad (66)$$

which with the limiting value $\hat{\mathcal{Q}} = 2$ as $\mathbf{p} \to 0$ agrees with the Pauli expression. A similar cancellation occurs for the terms involving $[\mathbf{p}^2, Y]$, but it leaves a scalar term, just as for the electric perturbations. Expanding the commutator of V with e_p, the terms linear in the field and correct to $\mathcal{O}(c^{-4})$ are

$$\frac{e}{m^2c^2}\hat{\mathcal{Q}}\boldsymbol{\sigma}\cdot(\nabla V)\times\mathbf{A}\hat{\mathcal{Q}} + \frac{e}{m^4c^4}\Bigg(Y\frac{1}{8e_p^3}\hat{\mathcal{Q}}[V,\mathbf{p}^2]\hat{\mathcal{Q}} + \hat{\mathcal{Q}}[\mathbf{p}^2,V]\hat{\mathcal{Q}}\frac{1}{8e_p^3}Y + Y\frac{2e_p+1}{4e_p^2(1+e_p)}\hat{\mathcal{Q}}\boldsymbol{\sigma}\cdot\mathbf{p}[V,\boldsymbol{\sigma}\cdot\mathbf{p}]\hat{\mathcal{Q}} + \hat{\mathcal{Q}}[\boldsymbol{\sigma}\cdot\mathbf{p},V]\boldsymbol{\sigma}\cdot\mathbf{p}\hat{\mathcal{Q}}\frac{2e_p+1}{4e_p^2(1+e_p)}Y + [\mathbf{p}^2,Y]\frac{2e_p^2+2e_p+1}{16e_p^3(1+e_p)}\hat{\mathcal{Q}}V\hat{\mathcal{Q}} + \hat{\mathcal{Q}}V\hat{\mathcal{Q}}\frac{2e_p^2+2e_p+1}{16e_p^3(1+e_p)}[Y,\mathbf{p}^2]\Bigg). \quad (67)$$

For a constant magnetic field, $[\mathbf{p}^2, Y]$ vanishes, and hence the complete linear term can be written (reinstating the commutator of V with e_p)

$$\frac{e}{2m^2c^2}\Bigg(\hat{\mathcal{Q}}\boldsymbol{\sigma}\times(\nabla V)\cdot\mathbf{B}\times\mathbf{r}\hat{\mathcal{Q}} + \mathbf{B}\cdot(\ell+\hbar\boldsymbol{\sigma})\frac{1}{2e_p^2}\hat{\mathcal{Q}}[V,e_p]\hat{\mathcal{Q}} + \hat{\mathcal{Q}}[e_p,V]\hat{\mathcal{Q}}\frac{1}{2e_p^2}\mathbf{B}\cdot(\ell+\hbar\boldsymbol{\sigma})\Bigg) + \frac{e}{m^4c^4}\Bigg(\mathbf{B}+(\ell+\hbar\boldsymbol{\sigma})\frac{2e_p+1}{4e_p^2(1+e_p)}\times\hat{\mathcal{Q}}\boldsymbol{\sigma}\cdot\mathbf{p}[V,\boldsymbol{\sigma}\cdot\mathbf{p}]\hat{\mathcal{Q}} + \hat{\mathcal{Q}}[\boldsymbol{\sigma}\cdot\mathbf{p},V]\boldsymbol{\sigma}\cdot\mathbf{p}\hat{\mathcal{Q}}\frac{2e_p+1}{4e_p^2(1+e_p)}\times\mathbf{B}\cdot(\ell+\hbar\boldsymbol{\sigma})\Bigg). \quad (68)$$

The only higher-order terms for a constant magnetic field are those involving derivatives of the potential, not of the field.

The remaining task is to consider the DK and BSS transformations. The terms of $\mathcal{O}(c^{-4})$ are reasonably easy to obtain because the terms added to the FPFW transformed Hamiltonian are already of $\mathcal{O}(c^{-4})$, and therefore only the lowest term is required. For the BSS transformation the term linear in the electric perturbation is simply

$$\frac{\hbar^2}{m^3c^4}(\nabla V)\cdot(\nabla W)\frac{1}{4e_p^2}. \quad (69)$$

Note that there is only a scalar term; the spin-dependent term vanishes. The Douglas–Kroll expression is a little more complicated, but follows straightforwardly from the definition of the term which is second order in the potential,

$$\frac{\hbar^2}{4m^3c^4}\hat{\mathcal{Q}}\Bigg[2\nabla\tilde{V}(\mathbf{p},\mathbf{p}')\cdot\nabla\tilde{W}(\mathbf{p}',\mathbf{p}'') + 2\nabla\tilde{W}(\mathbf{p},\mathbf{p}')\cdot\nabla\tilde{V}(\mathbf{p}',\mathbf{p}'') + \nabla\tilde{V}(\mathbf{p},\mathbf{p}')\frac{1}{e_{p'}}\cdot\nabla\tilde{W}(\mathbf{p}',\mathbf{p}'')e_{p''} + \nabla\tilde{W}(\mathbf{p},\mathbf{p}')\frac{1}{e_{p'}}\cdot\nabla\tilde{V}(\mathbf{p}',\mathbf{p}'')e_{p''} + e_p\nabla\tilde{V}(\mathbf{p},\mathbf{p}')\frac{1}{e_{p'}}\cdot\nabla\tilde{W}(\mathbf{p}',\mathbf{p}'') + e_p\nabla\tilde{W}(\mathbf{p},\mathbf{p}')\frac{1}{e_{p'}}\cdot\nabla\tilde{V}(\mathbf{p}',\mathbf{p}'')\Bigg]\hat{\mathcal{A}}'', \quad (70)$$

where $\tilde{W}$ is similarly defined to $\tilde{V}$. We may finally write for an example the BSS operator for a constant electric field, correct to $\mathcal{O}(c^{-4})$, as

$$W_1^{\mathrm{BSS,E,R}} = e\mathbf{E}\cdot\Bigg(\mathbf{r}+\frac{\hbar}{m^2c^2}\frac{\boldsymbol{\sigma}\times\mathbf{p}}{2e_p(1+e_p)} + \frac{\hbar^2}{m^3c^4}(\nabla V)\frac{1}{4e_p^2}\Bigg). \quad (71)$$

The magnetic terms of $\mathcal{O}(c^{-4})$ are zero, because they arise from the commutator $[V,\boldsymbol{\sigma}\cdot(\mathbf{p}+e\mathbf{A})] = [V,\boldsymbol{\sigma}\cdot\mathbf{p}]$. The lowest-order magnetic terms from the DK and BSS corrections to the FPFW transformed Hamiltonian arise at $\mathcal{O}(c^{-6})$ and have their origin in the kinematic factors $\hat{\mathcal{A}}'$ and ϵ_p. Thus the terms from the FPFW transformation are correct to $\mathcal{O}(c^{-4})$ for the magnetic perturbations.

Discussion and Conclusions

The derivation of property operators for the Douglas–Kroll and related transformations has been achieved to the order in c^{-2} to which the transformations are correct. For electric properties the implementation is simple and follows the same lines as for the nuclear potential. A general expression has been given by Kellö et al. [5]. The accuracy is also the same as for the nuclear potential: no further approximations have been introduced. From a formal point of view it is interesting to expand the electric properties in regularized powers of c^{-2}. These involve multiple commutators of the bare property operator with $\mathbf{p}^2$. For magnetic properties an expansion is necessary because the vector potential enters the Hamiltonian in the same way as the momentum, which appears in the transformed Hamiltonians in complicated functions of $\mathbf{p}^2$. These expansions will truncate for external fields, i.e., fields which transform as the regular SSHs, but for nuclear fields which transform as the irregular SSHs, the expansions do not truncate.

The Pauli expressions are all regularized in the FPFW transformation. External electric field operators have no scalar relativistic correction of $\mathcal{O}(c^{-2})$, but only a spin-dependent correction. Nuclear electric field operators have a Darwin-type correction. At $\mathcal{O}(c^{-4})$ there are both scalar and spin-dependent kinetic terms involving second to fourth derivatives of the property operator, and a scalar term involving the gradient of the potential and the gradient of the property. No spin-dependent terms involving the potential arise at $\mathcal{O}(c^{-4})$.

The same is true of the magnetic properties. The corrections linear in the field of $\mathcal{O}(c^{-2})$ are regularized versions of the Pauli operators. The cross-term between the field and the potential is spin-dependent: there is no scalar term. At fourth order there are both scalar and spin-dependent cross-terms. All of these arise from the FPFW transformation; the magnetic terms from the DK and BSS corrections to the FPFW Hamiltonian are $\mathcal{O}(c^{-6})$.

With the expressions for property operators presented in terms of the solid spherical harmonics and the procedures given for deriving property operators correct to any order in c^{-2}, it is hoped that what has been presented here will find its application in calculation of molecular properties with the inclusion of relativistic effects.

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