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COMMENT

Partial equivalence of the correct and incorrect versions of the Darwin term

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Abstract. The persistent appearance and use of an incorrect form of the Darwin term appearing in the non-relativistic approximation of the Dirac equation justifies an examination of when its use leads to no errors, as well as an examination of the reasons for its appearance.

The non-relativistic limit of the Dirac equation for a particle of charge q in an electromagnetic field produces a Schrödinger-Pauli wave equation for the large components of the Dirac wavefunction. To first order in v/c the usual magnetic and electric moment coupling terms appear, while to second order in v/c, not only is there the spin-orbit coupling term, H_{LS}, but also at second order the Darwin term.

In a static electric potential $\phi(\boldsymbol{r})$, the result obtained by Darwin, $H_{DD} = -2F(\boldsymbol{\nabla}\phi)\cdot\boldsymbol{\nabla}$, where $F = q\hbar^2/8m^2c^2$, is known to be incorrect although it and its incorrect derivation are quite often repeated. The correct result is $H_{CD} = F(\nabla^2\phi)$. To show the partial equivalence referred to, we consider matrix elements of these operators between two well behaved two-component wavefunctions. $U(\boldsymbol{r})$ and $V(\boldsymbol{r})$. Integrating the matrix element for H_{DD} by parts and setting the surface term to zero, we obtain

$$\begin{aligned}\langle U|H_{DD}|V\rangle &= -2F\int \mathrm{d}\tau U^\dagger[(\boldsymbol{\nabla}\phi)\cdot\boldsymbol{\nabla}]V \\ &= -2F\int \mathrm{d}S\,\boldsymbol{n}\cdot[U^\dagger(\boldsymbol{\nabla}\phi)V] + 2F\int \mathrm{d}\tau\,\boldsymbol{\nabla}\cdot[U^\dagger(\boldsymbol{\nabla}\phi)V] \\ &= 2F\int \mathrm{d}\tau\, U^\dagger(\nabla^2\phi)V + 2F\int \mathrm{d}\tau(\boldsymbol{\nabla}U^\dagger)\cdot(\boldsymbol{\nabla}\phi)V \\ &= 2\langle U|H_{CD}|V\rangle - \langle V|H_{DD}|U\rangle^*. \end{aligned} \tag{1}$$

Thus

$$\begin{aligned}\langle U|H_{CD}|V\rangle &= \tfrac{1}{2}[\langle U|H_{DD}|V\rangle + \langle V|H_{DD}|U\rangle^*] \\ &= \langle U|H_{DD} + H_{DD}^\dagger|V\rangle \end{aligned} \tag{2}$$

and therefore

$$H_{CD} = \tfrac{1}{2}(H_{DD} + H_{DD}^\dagger). \tag{3}$$

This result is a symptom of the fact that H_{DD} is incorrect because it is not Hermitian; furthermore the non-Hermitian nature of H_{DD} results from a faulty approximation

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procedure which replaces a non-Hermitian term in the total Hamiltonian by a Hermitian approximation to it, while leaving a compensating non-Hermitian term unchanged. We briefly discuss this point below. Although the result (3) shows that H_{CD} is the Hermitian part of H_{DD}, we note that matrix elements of H_{CD} are not the real parts of the corresponding matrix elements of H_{DD}, so that in general there is no easy way to escape from errors due to the use of the incorrect form.

However, setting $V = U$ in (2) we get the following relation:

$$\langle U|H_{CD}|U\rangle = [\langle U|H_{DD}|U\rangle + \text{CC}]$$
$$= Rl\langle U|H_{DD}|U\rangle \tag{4}$$

which is between expectation values if we assume that U is normalised as a two-component function. Since H_{DD} is real (in the algebraic sense) but not Hermitian, the expectation value $\langle U|H_{DD}|U\rangle$ is real if the function U has real components, when $\langle U|H_{CD}|U\rangle = \langle U|H_{DD}|U\rangle$. An instance of this occurs in treating the effect of the Darwin term as a perturbation to hydrogen-like atoms with central static Coulomb potential. Use of the incorrect version of the Darwin term gives (correctly) not only that the first-order energy perturbation is zero for other than S states, but also the correct result for S states.

Returning now to a discussion of the derivation of the Darwin term, the crucial approximating stage in obtaining a relativistic approximation to the Dirac equation occurs at the equation

$$[K - \boldsymbol{p}^2/2m + (\boldsymbol{\sigma}\cdot\boldsymbol{p})K(\boldsymbol{\sigma}\cdot\boldsymbol{p})/(4m^2c^2)]U = 0 \tag{5}$$

in which U consists of the two large components of the Dirac wavefunction, $\boldsymbol{p}$ is the operator for kinetic and total momentum (equal in zero magnetic field), $\boldsymbol{\sigma}$ is the vector of the Pauli matrices and $K \equiv E - mc^2 - q\phi$ can be regarded as an equivalent of the non-relativistic kinetic energy operator since E is the relativistic total energy eigenvalue. In equation (5) each term in the bracketed operator expression is Hermitian. Expansion of the third operator term which is of order v^2/c^2 with respect to each of the first two terms uses the result

$$(\boldsymbol{\sigma}\cdot\boldsymbol{p})K(\boldsymbol{\sigma}\cdot\boldsymbol{p}) = K\boldsymbol{p}^2 - q(\boldsymbol{p}\phi)\cdot\boldsymbol{p} - \mathrm{i}q\boldsymbol{\sigma}\cdot(\boldsymbol{p}\phi)\times\boldsymbol{p} \tag{6}$$

in which the last term is Hermitian and yields the spin-orbit coupling term in standard form if $\phi(\boldsymbol{r})$ becomes a central potential. Each of the first two terms in (6) is non-Hermitian but, of course, their sum is still Hermitian. Neglecting the third term in (6) we get

$$(K - \boldsymbol{p}^2/2m)U \cong 0. \tag{7}$$

Since the functions U span the manifold of all the allowed solutions, then over this manifold we have

$$K \cong \boldsymbol{p}^2/2m. \tag{8}$$

If one uses this approximation directly in (6) the non-Hermitian term $K\boldsymbol{p}^2$ is converted to $\boldsymbol{p}^4/2m$ which is Hermitian and one thereby arrives at a time-independent Schrödinger-Pauli equation with non-Hermitian Hamiltonian. Such an embarrassment is easily avoided by making the approximation (8) only in the symmetric part of the term $K\boldsymbol{p}^2$

of (6). Thus

$$\begin{aligned} K\boldsymbol{p}^2 &= \tfrac{1}{2}(K\boldsymbol{p}^2 + \boldsymbol{p}^2 K) + \tfrac{1}{2}(K\boldsymbol{p}^2 - \boldsymbol{p}^2 K) \\ &= \boldsymbol{p}^4/2m + \tfrac{1}{2}(K\boldsymbol{p}^2 - \boldsymbol{p}^2 K) \\ &= \boldsymbol{p}^4/2m + \tfrac{1}{2}q(\boldsymbol{p}^2\phi - \phi\boldsymbol{p}^2) \\ &= \boldsymbol{p}^4/2m - \tfrac{1}{2}q\hbar^2(\nabla^2\phi) + q(\boldsymbol{p}\phi)\cdot\boldsymbol{p}. \end{aligned} \tag{9}$$

Substitution of (9) into (5) gives

$$(E - mc^2)U = (q\phi + \boldsymbol{p}^2/2m - \boldsymbol{p}^4/8m^3c^2 + H_{CD} + H_{LS})\mathrm{U} \tag{10}$$

in which all the operator terms are Hermitian and in which the term H_{CD} appears as the correct form for the Darwin term. We see from (9) that the effect of the correct approximation is to directly exchange the non-Hermitian H_{DD} for the correct Hermitian Darwin term

$$H_{CD} = -\tfrac{1}{2}(q\hbar^2/8m^2c^2)(\nabla^2\phi). \tag{11}$$

Reference

Darwin C G 1928 *Proc. R. Soc.* A **118** 654-80