d. The Darwin Term

The spin-orbit interaction is proportional to $\mathbf{S} \cdot \mathbf{L}$. Therefore, there is no correction when the orbital angular momentum $\ell = 0$. There is, however, an additional correction term that pertains only when the orbital angular momentum is zero. It is referred to as the Darwin term.

The Darwin term is an additional perturbation that reveals itself in the hydrogen atom solution of the Dirac equation. Interestingly, the term obtained from the Dirac equation is

$$H_D = -\frac{\mathbf{P} \cdot [\mathbf{P}, \mathbf{V}]}{4m^2c^2} \quad \text{(tentative)}$$

This operator caused some trouble because it is not Hermetian. The difficulty is associated with the level of approximation made in the solution to the Dirac equation. It was the approximation that caused this term to be non-Hermetian. Darwin showed a way out. He properly symmetrized the operator.

$$H_D = -\frac{1}{8m^2c^2} \left\{ -2\mathbf{P} \cdot [\mathbf{P}, \mathbf{V}] + [\mathbf{P} \cdot \mathbf{P}, \mathbf{V}] \right\}$$

which reduces to

$$H_D = \frac{\hbar^2}{8m^2c^2} \nabla^2 V(r)$$

For the hydrogen atom $V(r) = -e^2/r$ so, since

$$\nabla^2 \left( \frac{1}{r} \right) = 4\pi \delta(r)$$

we have

$$H_D = \frac{e^2\hbar^2 \pi}{2m^2c^2} \delta(r)$$