The Pauli Hamiltonian

First let's define a set of 2x2 matrices called the Pauli spin matrices;

$$\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \; ; \; \boldsymbol{\sigma}_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \; ; \; \boldsymbol{\sigma}_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

And note for future reference that

$$\boldsymbol{\sigma}_x^2 = \boldsymbol{\sigma}_y^2 = \boldsymbol{\sigma}_z^2 = \mathbf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

and

$$\boldsymbol{\sigma}^2 = \boldsymbol{\sigma}_x^2 + \boldsymbol{\sigma}_y^2 + \boldsymbol{\sigma}_z^2 = 3\begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} = 3\mathbf{1}$$

We can rewrite $\boldsymbol{\alpha}_i$ & $\boldsymbol{\beta}$ matrices defined above in terms of these Pauli matrices as

$$\boldsymbol{\alpha}_x = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_x \\ \boldsymbol{\sigma}_x & \mathbf{0} \end{pmatrix}; \boldsymbol{\alpha}_y = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_y \\ \boldsymbol{\sigma}_y & \mathbf{0} \end{pmatrix} \; ; \; \boldsymbol{\alpha}_z = \begin{pmatrix} \mathbf{0} & \boldsymbol{\sigma}_z \\ \boldsymbol{\sigma}_z & \mathbf{0} \end{pmatrix}; \boldsymbol{\beta} = \begin{pmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{-1} \end{pmatrix}$$

If we then partition the four-element vector $\boldsymbol{\Psi}$ into two, two element vectors (called spinors)

$\boldsymbol{\Psi} = \begin{pmatrix} \boldsymbol{\varphi} \\ \boldsymbol{\chi} \end{pmatrix}$ where $\boldsymbol{\varphi} = \begin{pmatrix} u_1 \\ u_2 \end{pmatrix}$ & $\boldsymbol{\chi} = \begin{pmatrix} u_3 \\ u_4 \end{pmatrix}$ the Dirac equation may be written as

$$\begin{pmatrix} (E_0 - e\phi - E_R)\mathbf{1} & c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} \\ c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} & (-E_0 - e\phi - E_R)\mathbf{1} \end{pmatrix} \begin{pmatrix} \boldsymbol{\varphi} \\ \boldsymbol{\chi} \end{pmatrix} = 0$$

where $E_0 = mc^2$. We now partition the energy into the relativistic or rest mass contribution E_0

and the much smaller non-relativistic contribution E , $E_R = E_0 + E$ the Dirac equation becomes

$$\begin{pmatrix} (-E - e\phi)\mathbf{1} & c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} \\ c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} & -(2E_0 + e\phi + E)\mathbf{1} \end{pmatrix} \begin{pmatrix} \boldsymbol{\varphi} \\ \boldsymbol{\chi} \end{pmatrix} = 0$$

or

$$\begin{aligned} &(-E - e\phi)\boldsymbol{\varphi} + c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}}\boldsymbol{\chi} = 0 \\ &\textit{and} \\ &c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}}\boldsymbol{\varphi} - (2E_0 + e\phi + E)\boldsymbol{\chi} = 0 \end{aligned}$$

From the second of these equations we can write

$$\boldsymbol{\chi} = \left(2E_0 + e\phi + E\right)^{-1} c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}}\boldsymbol{\varphi}$$

Note that because the rest mass energy of the electron E_0 is $\sim 0.5\times10^6 eV$ the denominator is much larger than cp which is comparable to the kinetic energy of the electron. This means that $\boldsymbol{\chi}$ is, in some sense, much smaller than $\boldsymbol{\varphi}$. $\boldsymbol{\varphi}$ is called the large component of the wavefunction and $\boldsymbol{\chi}$ the small component.

Inserting this expression for $\boldsymbol{\chi}$ into the first results in

$$\left(-E - e\phi\right)\boldsymbol{\varphi} + c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}}\left(2E_0 + e\phi + E\right)^{-1} c\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}}\boldsymbol{\varphi} = 0$$

where we have been careful to note that $\phi(r)$ is a function of r and will be operated on by $\hat{\vec{p}}$. If we define the function $K(\phi) = \dfrac{2E_0}{2E_0 + e\phi + E}$ then the equation for the spinor $\boldsymbol{\varphi}$ becomes

$$\hat{\boldsymbol{H}}_{Dirac}\boldsymbol{\varphi} = \left(\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}}\frac{K(\phi)}{2m}\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} - e\phi(r)\mathbf{1}\right)\boldsymbol{\varphi} = E\boldsymbol{\varphi}$$

Note that because $K(\phi)$ depends on E this is a pseudo eigenvalue problem. Also note that up to this point in our development this equation for $\boldsymbol{\varphi}$ is exact. To proceed we note the identity

$$(\vec{\boldsymbol{\sigma}} \bullet \vec{A})(\vec{\boldsymbol{\sigma}} \bullet \vec{B}) = (\vec{A} \bullet \vec{B})\mathbf{1} + i\vec{\boldsymbol{\sigma}} \bullet (\vec{A} \times \vec{B})$$

So with $\vec{A} = \vec{p}$ & $\vec{B} = K(\phi)\vec{p}$ we have

$$\hat{\boldsymbol{H}}_{Dirac}\boldsymbol{\varphi} = \left(\frac{1}{2m}\hat{\vec{p}} \bullet K(\phi)\hat{\vec{p}}\mathbf{1} + \frac{i}{2m}\vec{\boldsymbol{\sigma}} \bullet (\hat{\vec{p}} \times K(\phi)\hat{\vec{p}}) - e\phi(r)\right)\boldsymbol{\varphi} = E\boldsymbol{\varphi}$$

To simplify the Dirac Hamiltonian we note that when the operator $\hat{\vec{p}} \bullet K(\phi)\hat{\vec{p}}$ operates on an arbitrary spinor, $\begin{pmatrix} f \\ g \end{pmatrix}$ it operates on each component and so we can consider its effect on each spatial function independently. Consider

$$\hat{\vec{p}} \bullet K(\phi)\hat{\vec{p}}f = -\hbar^2\nabla_\alpha(K\nabla_\alpha f) = -\hbar^2\left(K\nabla^2 f + \nabla_\alpha K \bullet \nabla_\alpha f\right)$$

where we sum over repeated Greek indices.

Now $\nabla_\alpha K = \dfrac{\partial K}{\partial\phi}\nabla_\alpha\phi = -F_\alpha\dfrac{\partial K}{\partial\phi}$ where F_α is the α component of the electric field due to the nuclear charge and so

$$\left(\hat{\vec{p}} \bullet K(\phi)\hat{\vec{p}}\right)f = K(\phi)\hat{\vec{p}}^2 f + i\hbar\frac{\partial K}{\partial\phi}\left(\vec{F} \bullet \hat{\vec{p}}\right)f$$

with the same result for g the other scalar component of the spinor and so

$$\hat{\vec{p}} \bullet K(\phi)\hat{\vec{p}} = K(\phi)\hat{\vec{p}}^2 + i\hbar\frac{\partial K}{\partial\phi}\left(\vec{F} \bullet \hat{\vec{p}}\right)$$

Now consider the term $\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} \times K\hat{\vec{p}}$

First allow $\left(\hat{\vec{p}} \times K\hat{\vec{p}}\right)_\alpha$ to operate on an arbitrary function f

$$\left(\hat{\vec{p}} \times K\hat{\vec{p}}\right)_\alpha f = -\hbar^2\varepsilon_{\alpha\beta\gamma}\nabla_\beta\left(K\nabla_\gamma f\right) = -\hbar^2\varepsilon_{\alpha\beta\gamma}\left(K\nabla_\beta\nabla_\gamma f + \nabla_\beta K\nabla_\gamma f\right)$$

and since $\varepsilon_{\alpha\beta\gamma}\nabla_\beta\nabla_\gamma f$ is identically zero we have

$$\left(\hat{\vec{p}} \times K\hat{\vec{p}}\right)_\alpha f = -\hbar^2\varepsilon_{\alpha\beta\gamma}\nabla_\gamma f\nabla_\beta K = -\hbar^2\frac{\partial K}{\partial\phi}\varepsilon_{\alpha\beta\gamma}\nabla_\beta\phi\nabla_\gamma f = -i\hbar\frac{\partial K}{\partial\phi}\varepsilon_{\alpha\beta\gamma}\nabla_\beta\phi\hat{p}_\gamma f$$

and since $\nabla_\beta\phi = -F_\beta$ we have

$$\left(\hat{\vec{p}} \times K\hat{\vec{p}}\right)_\alpha = i\hbar\frac{\partial K}{\partial\phi}\varepsilon_{\alpha\beta\gamma}F_\beta\hat{p}_\gamma = i\hbar\frac{\partial K}{\partial\phi}\left(\vec{F} \times \hat{\vec{p}}\right)_\alpha$$

and so

$$\vec{\boldsymbol{\sigma}} \bullet \hat{\vec{p}} \times K\hat{\vec{p}} = i\hbar\frac{\partial K}{\partial\phi}\vec{\boldsymbol{\sigma}} \bullet \vec{F} \times \hat{\vec{p}}\,.$$

So now the Dirac Hamiltonian operating on the two component spinor becomes

$$\hat{\boldsymbol{H}}_{Dirac} = \frac{\hat{\vec{p}}^2}{2m} - e\phi + \left(K(\phi) - 1\right)\frac{\hat{\vec{p}}^2}{2m} + \frac{i\hbar}{2m}\frac{\partial K}{\partial\phi}\vec{F} \bullet \hat{\vec{p}} - \frac{\hbar}{2m}\frac{\partial K}{\partial\phi}\vec{\boldsymbol{\sigma}} \bullet \vec{F} \times \hat{\vec{p}}$$

Once again we note that this is still exact, i.e., correct to all orders of V/c.

The first two terms constitute the Schrodinger Hamiltonian

$$\hat{\boldsymbol{H}}_{Schrodinger} = \frac{\hat{\vec{p}}^2}{2m} - e\phi$$

The next term corrects for the variation in the mass of the electron with its speed and is called the mass-velocity term

$$\hat{H}_{MV} = \left(K(\phi) - 1\right)\frac{\hat{\vec{p}}^2}{2m}$$

Following this we have the Darwin term which has no classical interpretation

$$\hat{H}_{Darwin} = \frac{i\hbar}{2m}\frac{\partial K}{\partial\phi}\vec{F} \bullet \hat{\vec{p}}$$

And lastly we have the spin-orbit term

$$\hat{H}_{SO} = -\frac{\hbar}{2m}\frac{\partial K}{\partial \phi}\vec{\boldsymbol{\sigma}} \bullet \vec{F} \times \hat{\vec{p}}$$

Pauli Matrices and Spin

$\hat{H}_{SO}$ involves the 2x2 Pauli matrix $\vec{\boldsymbol{\sigma}}$ so let look at some of its properties, in particular the commutation relations among its x, y, z components. Consider the commutator

$$\left[\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y\right] = \boldsymbol{\sigma}_x\boldsymbol{\sigma}_y - \boldsymbol{\sigma}_y\boldsymbol{\sigma}_x$$

and using the definitions given above

$$\boldsymbol{\sigma}_x\boldsymbol{\sigma}_y = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}\begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} = \begin{pmatrix} i & 0 \\ 0 & -i \end{pmatrix} = i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = i\boldsymbol{\sigma}_z$$

while

$$\boldsymbol{\sigma}_y\boldsymbol{\sigma}_x = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} = \begin{pmatrix} -i & 0 \\ 0 & i \end{pmatrix} = -i\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} = -i\boldsymbol{\sigma}_z$$

so

$$\left[\boldsymbol{\sigma}_x, \boldsymbol{\sigma}_y\right] = \boldsymbol{\sigma}_x\boldsymbol{\sigma}_y - \boldsymbol{\sigma}_y\boldsymbol{\sigma}_x = 2i\boldsymbol{\sigma}_z$$

In a similar fashion we find

$$\left[\boldsymbol{\sigma}_y, \boldsymbol{\sigma}_z\right] = 2i\boldsymbol{\sigma}_x \quad \& \quad \left[\boldsymbol{\sigma}_z, \boldsymbol{\sigma}_x\right] = 2i\boldsymbol{\sigma}_y$$

These commutator's are very similar to those that define an angular momentum vector $\hat{\vec{J}}$ i.e.,

$\left[\hat{J}_x, \hat{J}_y\right] = i\hbar\hat{J}_z$ plus cyclic permutations of the indicies. If we define $\hat{\vec{\boldsymbol{S}}} = \frac{\hbar}{2}\boldsymbol{\sigma}$ so that

$\hat{\boldsymbol{S}}_\alpha = \frac{\hbar}{2}\boldsymbol{\sigma}_\alpha \;, \boldsymbol{\alpha} = x, y, z$ these operators have the commutators

$$\left[\hat{\boldsymbol{S}}_x, \hat{\boldsymbol{S}}_y\right] = i\hbar\hat{\boldsymbol{S}}_z$$

and are therefore angular momentum operators and in particular spin angular momentum. We see that since $\hat{\boldsymbol{S}}^2 = \hat{\boldsymbol{S}}_x^2 + \hat{\boldsymbol{S}}_y^2 + \hat{\boldsymbol{S}}_z^2 = \frac{3}{4}\hbar^2\boldsymbol{1}$ it commutes with each of its components and as usual we select $\hat{\boldsymbol{S}}_z \;\&\; \hat{\boldsymbol{S}}^2$ to have simultaneous eigenfunctions. The eigenfunctions of $\hat{\boldsymbol{S}}_z = \frac{\hbar}{2}\begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$ are

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix} \& \begin{pmatrix} 0 \\ 1 \end{pmatrix} \text{ with eigenvalues } \pm\frac{\hbar}{2}$$

and

$$\hat{\boldsymbol{S}}^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 1 \\ 0 \end{pmatrix} = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 \begin{pmatrix} 1 \\ 0 \end{pmatrix}$$

and

$$\hat{\boldsymbol{S}}^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{3\hbar^2}{4} \begin{pmatrix} 0 \\ 1 \end{pmatrix} = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

We will often abbreviate $\begin{pmatrix} 1 \\ 0 \end{pmatrix} \& \begin{pmatrix} 0 \\ 1 \end{pmatrix}$ as $\boldsymbol{\alpha} \,\&\, \boldsymbol{\beta}$ respectfully (remember these are not the Dirac matrices $\boldsymbol{\alpha} \,\&\, \boldsymbol{\beta}$) and write

$$\hat{S}_z \boldsymbol{\alpha} = \frac{\hbar}{2}\boldsymbol{\alpha} \;\;\&\;\; \hat{S}_z \boldsymbol{\beta} = -\frac{\hbar}{2}\boldsymbol{\beta} \text{ and}$$

$$\hat{S}^2 \boldsymbol{\alpha} = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 \boldsymbol{\alpha} = \frac{3\hbar^2}{4}\boldsymbol{\alpha} \,\&\, \hat{S}^2 \boldsymbol{\beta} = \frac{1}{2}\left(\frac{1}{2}+1\right)\hbar^2 \boldsymbol{\beta} = \frac{3\hbar^2}{4}\boldsymbol{\beta}.$$

Since $\vec{F} = \dfrac{e^2 Z\, \vec{r}}{4\boldsymbol{\pi\varepsilon}_0 r^3}$ and $\hat{\vec{\boldsymbol{S}}} = \dfrac{\hbar}{2}\vec{\boldsymbol{\sigma}}$ we can write

$$\hat{H}_{SO} = -\frac{\hbar}{2m}\frac{\partial K}{\partial \phi}\vec{\boldsymbol{\sigma}} \bullet \vec{F} \times \hat{\vec{p}} = -\frac{Ze}{4\boldsymbol{\pi\varepsilon}_0 r^3 m}\frac{\partial K}{\partial \phi}\hat{\vec{S}} \bullet \vec{r} \times \hat{\vec{p}} = -\frac{Ze}{4\boldsymbol{\pi\varepsilon}_0 r^3 m}\frac{\partial K}{\partial \phi}\hat{\vec{S}} \bullet \hat{\vec{L}}$$

This is the spin-orbit term and it represents the interaction of the electrons spin with the magnetic field due to the nuclear motion.

Pauli Hamiltonian Correct to order $(V/c)^2$

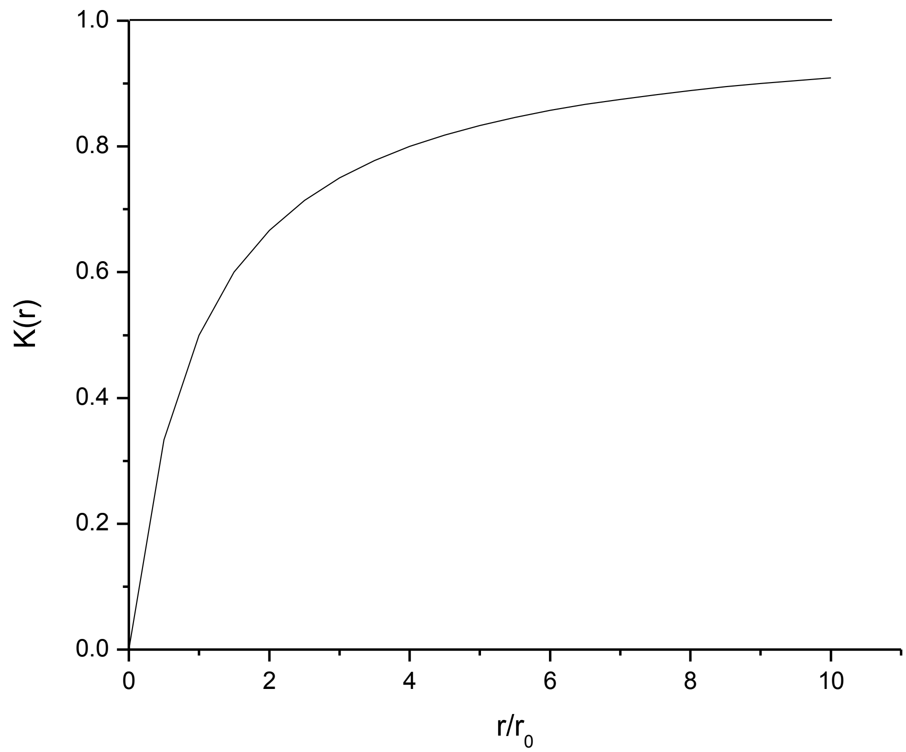
We will now develop an approximate Hamiltonian correct to order $\left(V/c\right)^2$. Lets look again at $K(\phi)$. Classically we have

$$K(\phi) = \frac{2mc^2}{2mc^2 + e\phi + E} = \frac{1}{1 + \dfrac{e^2 Z}{8\pi\varepsilon_0 mc^2 r} + \dfrac{E}{2mc^2}} = \frac{1}{1 + \dfrac{r_0}{r} + \dfrac{E}{2mc^2}}$$

Where $r_0 = \dfrac{e^2 Z}{8\pi\varepsilon_0 mc^2}$ is approximately the size of a nuclear diameter ≈10^{-15} M

and since the rest mass energy of the electron is approximately 0.5 x 10^6 ev and *E* is about -13.6 eV,

the ratio $\dfrac{E}{2mc^2} : 10^{-5}$. From the plot of $K(r)$ we see that one can expect the effects of $K(r)$ to be important close to the nucleus.



Lets consider the mass-velocity term and note that we can write

$$K(\phi) = \frac{2mc^2}{2mc^2 + e\phi + E} = \frac{1}{1 + \dfrac{e\phi + E}{2mc^2}} = \frac{1}{1 + \dfrac{p^2/2m}{2mc^2}}$$

and since the kinetic energy of the electron is considerably smaller than its rest mass we may write

$K(\phi) \sim 1 - \dfrac{\vec{p}^2}{4m^2c^2} + \cdots$ so

$$\hat{H}_{MV} = -\frac{\hat{\vec{p}}^4}{8m^3c^2} = -\frac{\hbar^4 \nabla^4}{8m^3c^2}$$

where ∇^4 means we operate with ∇^2 twice. Now for the Darwin term

$$\hat{H}_{Darwin} = \frac{i\hbar}{2m}\frac{\partial K}{\partial \phi}\vec{F} \bullet \hat{\vec{p}}$$

Since $\frac{\partial K}{\partial \phi}$ is equal to $-\frac{eK^2}{2mc^2}$, $\vec{F} = -\nabla \phi$ and $\hat{\vec{p}} = -i\hbar\nabla$ have

$$\hat{H}_{Darwin} = \frac{\hbar^2 e^2 K^2(\phi)}{(2mc)^2}\nabla\phi \bullet \nabla = \frac{\hbar^2 e}{(2mc)^2}\nabla\phi \bullet \nabla$$

where we approximate $K^2(\phi)$ as 1. Matrix elements of this operator involve $\left\langle \psi \middle| \nabla\phi \bullet \nabla \middle| \psi \right\rangle$ which can be rewritten by noting

$$\left\langle \psi \middle| \nabla^2 \middle| \phi\psi \right\rangle = \left\langle \psi \middle| \nabla \bullet \left(\psi\nabla\phi + \phi\nabla\psi \right) \right\rangle = \left\langle \psi \middle| \nabla^2\phi \middle| \psi \right\rangle + 2\left\langle \psi \middle| \nabla\phi \bullet \nabla \middle| \psi \right\rangle + \left\langle \psi\phi \middle| \nabla^2 \middle| \psi \right\rangle$$

Since ∇^2 is Hermitian the left hand term is cancelled by the last on the right leaving

$\left\langle \psi \middle| \nabla\phi \bullet \nabla \middle| \psi \right\rangle = -\frac{1}{2}\left\langle \psi \middle| \nabla^2\phi \middle| \psi \right\rangle$ and so

$\hat{H}_{Darwin} = \frac{-\hbar^2 e}{2(2mc)^2}\nabla^2\phi$ and since $\phi = \frac{eZ}{4\pi\varepsilon_0 r}$ we have

$$\hat{H}_{Darwin} = \frac{-\hbar^2 e^2 Z}{8\pi\varepsilon_0 (2mc)^2}\nabla^2 \frac{1}{r} = \frac{\hbar^2 e^2 Z \delta^3(\vec{r})}{2\varepsilon_0 (2mc)^2}$$

Where $\delta^3(\vec{r})$ is the three dimensional Dirac delta function defined as

$\delta^3\left(\vec{r}\right) = \frac{\delta(r)}{4\pi r^2}$ where $\int_0^\infty \delta(r)dr = 1$ and $\int_0^\infty \delta(r)f(r)dr = f(0)$

Now for the spin-orbit term.

$$\hat{H}_{SO} = -\frac{Ze}{4\boldsymbol{\pi\varepsilon}_0 r^3 m}\frac{\partial K}{\partial \phi}\hat{\vec{S}} \bullet \hat{\vec{L}}$$

Since $\frac{\partial K}{\partial \phi} = -\frac{eK^2}{2mc^2} \approx -\frac{e}{2mc^2}$ we have

$$\hat{H}_{SO} = -\frac{Ze^2}{(mc)^2 8\boldsymbol{\pi\varepsilon}_0 r^3}\hat{\vec{S}} \bullet \hat{\vec{L}}$$

And so we have the Pauli Hamiltonian

$$\hat{H}_{Pauli} = \hat{H}^0_{Shrodinger} + \hat{H}_{mv} + \hat{H}_D + \hat{H}_{SO}$$