

Chapter 4

Spin-Orbit Coupling

4.1 Addition of Angular Momenta

4.1.1 Alternate set of angular momentum operators

We consider two independent systems that each carries angular momenta (each could be either orbital angular momentum or spin). Before the two systems are coupled, each system is described by the angular momentum operators $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ and their eigenstates $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ satisfying the conditions

$$\begin{aligned}\hat{\mathbf{J}}_i^2|j_i, m_i\rangle &= \hbar^2 j_i(j_i + 1)|j_i, m_i\rangle, \\ \hat{J}_{iz}|j_i, m_i\rangle &= \hbar m_i|j_i, m_i\rangle, \\ \hat{J}_{i\pm}|j_i, m_i\rangle &= \hbar\sqrt{j_i(j_i + 1) - m_i(m_i \pm 1)}|j_i, m_i \pm 1\rangle,\end{aligned}\tag{4.1}$$

for $i = 1, 2$. When we consider the combination of these two systems, the basis of the combined system is created by

$$|j_1, j_2; m_1, m_2\rangle = |j_1, m_1\rangle \otimes |j_2, m_2\rangle,\tag{4.2}$$

where \otimes indicates the tensor product of two states that describe the two independent systems.

When the total angular momentum of the two systems is considered, it is described by the sum of the two angular momentum operators $\hat{\mathbf{J}} = \hat{\mathbf{J}}_1 + \hat{\mathbf{J}}_2$. Because the two systems are independent, the operators $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ commute with each other, and the components of each system satisfies the commutation relations of the angular momentum operator. It is easy to verify that the components of the total angular momentum operator $\hat{\mathbf{J}}$ also satisfies the commutation relationship

$$[\hat{J}_i, \hat{J}_j] = i\hbar\varepsilon_{ijk}\hat{J}_k.\tag{4.3}$$

We now look for four independent operators that commute with each other that includes the operators $\hat{\mathbf{J}}^2$ and \hat{J}_z , to provide an alternative description of the combined system as compared to the four commuting operators $\{\hat{\mathbf{J}}_1^2, \hat{J}_{1z}, \hat{\mathbf{J}}_2^2, \hat{J}_{2z}\}$.

Since $\hat{\mathbf{J}}_1$ and $\hat{\mathbf{J}}_2$ each commute with $\hat{\mathbf{J}}_1^2$ and $\hat{\mathbf{J}}_2^2$, so does $\hat{\mathbf{J}}$. More specifically, we note that $\hat{\mathbf{J}}^2$ and \hat{J}_z both commute with the operators $\hat{\mathbf{J}}_1^2$ and $\hat{\mathbf{J}}_2^2$;

$$\begin{aligned} [\hat{\mathbf{J}}^2, \hat{\mathbf{J}}_1^2] &= [\hat{\mathbf{J}}^2, \hat{\mathbf{J}}_2^2] = 0, \\ [\hat{J}_z, \hat{\mathbf{J}}_1^2] &= [\hat{J}_z, \hat{\mathbf{J}}_2^2] = 0. \end{aligned} \quad (4.4)$$

The operators \hat{J}_{1z} and \hat{J}_{2z} commute with the operator $\hat{J}_z = \hat{J}_{1z} + \hat{J}_{2z}$. However, since

$$\hat{\mathbf{J}}^2 = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{\mathbf{J}}_1 \cdot \hat{\mathbf{J}}_2 = \hat{\mathbf{J}}_1^2 + \hat{\mathbf{J}}_2^2 + 2\hat{J}_{1z}\hat{J}_{2z} + \hat{J}_{1+}\hat{J}_{2-} + \hat{J}_{1-}\hat{J}_{2+}, \quad (4.5)$$

the operators \hat{J}_{1z} and \hat{J}_{2z} do not commute with $\hat{\mathbf{J}}^2$. So, the four operators $\{\hat{\mathbf{J}}_1^2, \hat{\mathbf{J}}_2^2, \hat{\mathbf{J}}^2, \hat{J}_z\}$ commute with each other, and forms a natural basis with which to describe the total angular momentum of the combined system.

4.1.2 Addition rule for the angular momentum states

Classically, angular momentum is a vector, so when two angular momenta \vec{L}_1 and \vec{L}_2 are added together, the magnitude of the resulting angular momentum can be between $|\vec{L}_1 - \vec{L}_2|$ when the two vectors are aligned in opposite directions, and $|\vec{L}_1 + \vec{L}_2|$ when the two vectors are aligned in the same direction. Quantum mechanically, the “magnitude” of the angular momentum operator $\hat{\mathbf{J}}$ is roughly represented by its eigenvalue j , so when the two angular momentum operators $\hat{\mathbf{J}}_1$ with eigenvalue j_1 and $\hat{\mathbf{J}}_2$ with eigenvalue j_2 are added (without loss of generality, we assume $j_1 \geq j_2$), one can speculate that the resulting operator $\hat{\mathbf{J}}$ will have its eigenvalue j between the values $j_1 - j_2$ and $j_1 + j_2$. It turns out that this speculation is exactly true, and the addition rule for angular momentum can be stated as follows:

- When two systems each with angular momentum of eigenvalues j_1 and j_2 are added, the angular momentum eigenvalue of the added system runs from $|j_1 - j_2|$ to $j_1 + j_2$ in increments of 1, and
- For each resulting j value, m_j runs from $-j$ to j in increments of 1, *i.e.*, $m_j = -j, -j + 1, \dots, j - 1, j$.

Although a formal proof is quite complicated, we provide some examples in the next section to illustrate the results. We note that the total number of states in the two systems is $(2j_1 + 1)(2j_2 + 1)$, since the degeneracy (total number of m_j states) are $2j_1 + 1$ for the first system and $2j_2 + 1$ for the second system, respectively. In the description of the combined system, the total number of m_j states is $2j + 1$ for each j value, so the total number of states is given by

$$\begin{aligned} N &= \sum_{i=j_1-j_2}^{j_1+j_2} (2i + 1) = \sum_{i=0}^{j_1+j_2} (2i) - \sum_0^{j_1-j_2-1} (2i) + (j_1 + j_2) - (j_1 - j_2) + 1 \\ &= (j_1 + j_2 + 1)(j_1 + j_2) - (j_1 - j_2)(j_1 - j_2 - 1) + 2j_2 + 1 \\ &= (j_1 + j_2)^2 - (j_1 - j_2)^2 + 2j_1 + 2j_2 + 1 = (2j_1 + 1)(2j_2 + 1), \end{aligned} \quad (4.6)$$

matching the total number of states in the description of individual systems.

4.1.3 Addition of two spins

In this section, we consider addition of angular momentum for two spin 1/2 particles. In the uncoupled representation, the four quantum numbers are $\{\hat{\mathbf{S}}_1^2, \hat{S}_{1z}, \hat{\mathbf{S}}_2^2, \hat{S}_{2z}\}$, and the four possible states are

$$|\xi\rangle = \left| \frac{1}{2}, \frac{1}{2}, \pm \frac{1}{2}, \pm \frac{1}{2} \right\rangle. \quad (4.7)$$

These corresponds to the four basis spin states $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$.

In the coupled representation, the states are simultaneous eigenstates of the four operators $\{\hat{\mathbf{S}}^2, \hat{S}_z, \hat{\mathbf{S}}_1^2, \hat{\mathbf{S}}_2^2\}$, where

$$\begin{aligned} \hat{\mathbf{S}}^2 &= (\hat{\mathbf{S}}_1 + \hat{\mathbf{S}}_2)^2 = \hat{\mathbf{S}}_1^2 + \hat{\mathbf{S}}_2^2 + 2\hat{\mathbf{S}}_1 \cdot \hat{\mathbf{S}}_2, \\ \hat{S}_z &= \hat{S}_{1z} + \hat{S}_{2z}. \end{aligned} \quad (4.8)$$

First, we note that the values of s , eigenvalue of the $\hat{\mathbf{S}}^2$ operator, greater than 1 are not possible. This is because that would require m_s (eigenvalue of the operator \hat{S}_z) of value larger than 1, but $m_s = m_{1s} + m_{2s}$ and both m_{1s} and m_{2s} can only take values of $\pm 1/2$.

Next, we note that $s = 1$ is possible, since $m_s = 1$ is possible. Since $m_s = 1$ can only happen when $m_{1s} = m_{2s} = +1/2$, this state is not degenerate. From this argument, we note that $|s = 1, m_s = 1\rangle = |\uparrow\uparrow\rangle$.

Applying the total spin lowering operator $\hat{S}_- = \hat{S}_{1-} + \hat{S}_{2-}$ yields, using Eq. 4.1,

$$\begin{aligned} \hat{S}_- |s = 1, m_s = 1\rangle &= \hbar\sqrt{2} |s = 1, m_s = 0\rangle \\ &= (\hat{S}_{1z} + \hat{S}_{2z}) |\uparrow\uparrow\rangle = \hbar\sqrt{\frac{1}{2}\frac{3}{2} + \frac{1}{2}\frac{1}{2}} (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) = |\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle. \end{aligned} \quad (4.9)$$

So, we conclude that $|s = 1, m_s = 0\rangle = (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$.

Applying the total spin lowering operator once again on this state gives

$$\begin{aligned} \hat{S}_- |s = 1, m_s = 0\rangle &= \hbar\sqrt{2} |s = 1, m_s = -1\rangle \\ &= \frac{1}{\sqrt{2}} (\hat{S}_{1z} + \hat{S}_{2z}) (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ &= \frac{\hbar}{\sqrt{2}} \sqrt{\frac{1}{2}\frac{3}{2} + \frac{1}{2}\frac{1}{2}} (|\downarrow\downarrow\rangle + |\downarrow\downarrow\rangle) = \hbar\sqrt{2} |\downarrow\downarrow\rangle, \end{aligned} \quad (4.10)$$

and therefore $|s = 1, m_s = -1\rangle = |\downarrow\downarrow\rangle$, as expected. These three states form the **spin triplet states**

$$\begin{aligned} |s = 1, m_s = 1\rangle &= |\uparrow\uparrow\rangle \\ |s = 1, m_s = 0\rangle &= (|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2} \\ |s = 1, m_s = -1\rangle &= |\downarrow\downarrow\rangle \end{aligned} \quad (4.11)$$

The next possible s value is $s = 0$, accompanied by $m_s = 0$ as the only possible m_s value. This fourth state is formed by a linear superposition of the four basis spin states $\{|\uparrow\uparrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, |\downarrow\downarrow\rangle\}$, and is orthogonal to all three triplet states in Eq. 4.11. We see that this fourth state cannot contain $|\uparrow\uparrow\rangle$ nor $|\downarrow\downarrow\rangle$ states, and therefore has to be a linear superposition of only $|\uparrow\downarrow\rangle$ and $|\downarrow\uparrow\rangle$. In order for such a superposition state to be orthogonal to the $|s = 1, m_s = 0\rangle$ state, we derive the final state, known as the **singlet state**, as

$$|s = 0, m_s = 0\rangle = (|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}. \quad (4.12)$$

4.1.4 Clebsch-Gordan coefficients

The basis state $|j, m_j\rangle$ of the coupled system can be expressed in a linear superposition of the uncoupled basis states $|j_1, j_2; m_1, m_2\rangle$, as by definition, basis states span the entire Hilbert space for the quantum system. By noting that the identity operator is given by the sum of the outer product of all basis states

$$\hat{I} = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2|, \quad (4.13)$$

we can express the basis states of the coupled system as

$$|j, m_j\rangle = \sum_{m_1=-j_1}^{j_1} \sum_{m_2=-j_2}^{j_2} |j_1, j_2; m_1, m_2\rangle \langle j_1, j_2; m_1, m_2|j, m_j\rangle. \quad (4.14)$$

Inner product of two quantum states is a complex number, and the complex numbers $\langle j_1, j_2; m_1, m_2|j, m_j\rangle$ are called *Clebsch-Gordan coefficients*.

4.2 Spin-Orbit Coupling

4.2.1 Orbiting spins and the term notation

For the case of a hydrogen atom, an electron with spin $1/2$ orbits around the nucleus (proton), itself with spin $1/2$. For now, we ignore the nuclear spin, and focus on the interaction between the electron spin and its orbit around the nucleus. This leads to fine structures in the atomic spectrum. The interaction between the resulting energy levels with the nuclear spin is called the hyperfine interaction: this interaction is typically several orders of magnitude smaller, and we will consider that in later chapters.

The total angular momentum $\hat{\mathbf{J}}$ under these conditions arise from two sources of angular momenta, the spin $\hat{\mathbf{S}}$ and the orbital angular momentum $\hat{\mathbf{L}}$: $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$. The operators $\hat{\mathbf{L}}$ and $\hat{\mathbf{S}}$ commute, as they are completely independent degrees of freedom. The eigenstates we consider are simultaneous eigenstates of the operators $\{\hat{\mathbf{J}}^2, \hat{J}_z, \hat{\mathbf{L}}^2, \hat{\mathbf{S}}^2\}$, which all commute with each other. The eigenvalue equations are given by

$$\begin{aligned} \hat{\mathbf{J}}^2|j, m_j, l, s\rangle &= \hbar^2 j(j+1)|j, m_j, l, s\rangle \\ \hat{J}_z|j, m_j, l, s\rangle &= \hbar m_j|j, m_j, l, s\rangle \\ \hat{\mathbf{L}}^2|j, m_j, l, s\rangle &= \hbar^2 l(l+1)|j, m_j, l, s\rangle \\ \hat{\mathbf{S}}^2|j, m_j, l, s\rangle &= \hbar^2 s(s+1)|j, m_j, l, s\rangle, \end{aligned} \quad (4.15)$$

where j runs from $|l-s|$ to $l+s$, and for each j , m_j runs from $-j$ to j . We note that

$$\begin{aligned} \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}|j, m_j, l, s\rangle &= \frac{1}{2}(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2)|j, m_j, l, s\rangle \\ &= \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]|j, m_j, l, s\rangle. \end{aligned} \quad (4.16)$$

For $s < l$, there are $(2s+1)$ possible values of j : the total number of possible j values is called *multiplicity*. For one-electron atom (such as the hydrogen atom) with $s = 1/2$, there

are two possible values of j for $l \geq 1$, $j = l - \frac{1}{2}$ and $j = l + \frac{1}{2}$, and the multiplicity is $2 \cdot \frac{1}{2} + 1 = 2$. The spin-orbit coupling of the atomic levels are typically denoted using the *term notation* (or *term symbol*)

$${}^{2s+1}L_j, \quad (4.17)$$

where $L = S, P, D, F, \dots$ for $l = 0, 1, 2, 3, \dots$. For example, the doublet P states corresponding to $l = 1$ are ${}^2P_{1/2}$ and ${}^2P_{3/2}$ states, and the doublet D states corresponding to $l = 2$ are ${}^2D_{3/2}$ and ${}^2D_{5/2}$ states.

4.2.2 Spin-orbit coupling: induced magnetic field

In a one-electron atom where there is one electron in the outer-most orbit, the spin of this valence electron interacts with the shielded Coulomb field due to the nucleus and the remaining (core) electrons forming a closed shell. Examples of such atoms are alkali atoms in the first column of the periodic table, or singly ionized atomic ions of atoms that have filled s states (such as the alkali-earth atoms in the second column of the periodic table). In these atoms, the spin-orbit coupling modifies the basic structure of the hydrogen-like atom in two ways that have roughly the same order-of-magnitude correction: one by the induced magnetic field by the spin, and the other by the relativistic correction.

If an observer is moving with a velocity \vec{v} in an electric field of \vec{E} , the observer experiences magnetic field given by

$$\vec{B} = -\gamma \frac{\vec{v}}{c} \times \vec{E}, \quad (4.18)$$

where c is the speed of light in vacuum, $\gamma^{-2} = 1 - \beta^2$, and $\beta = |\vec{v}/c|$. To first order in β , we get

$$\vec{B} \simeq -\frac{1}{c} \vec{v} \times \vec{E} = -\frac{\vec{p}}{m_e c} \times \vec{E}. \quad (4.19)$$

If the observer is an electron, its magnetic moment interacts with this “induced” magnetic field via the interaction Hamiltonian

$$\hat{H}' = -\frac{1}{2} \vec{\mu} \cdot \vec{B} = \frac{1}{2} \vec{\mu} \cdot \left(\frac{\vec{v}}{c} \times \vec{B} \right) = -\frac{1}{2} \frac{\vec{\mu}}{m_e c} (\vec{E} \times \vec{p}). \quad (4.20)$$

Here, the factor of $1/2$ in front is called the Thomas factor. Since for electric field created by the nucleus arises from the central potential and only has a radial component, we can express it as $\vec{E} = \vec{E}_r = -\frac{d\phi(r)}{dr} \hat{r}$, that leads to

$$\hat{H}' = -\frac{1}{2} \frac{\vec{\mu}}{m_e c} \left[\frac{1}{r} \frac{d}{dr} \phi(r) \right] (\vec{r} \times \vec{p}) \cdot \vec{\mu} \equiv f(r) \hat{\mathbf{L}} \cdot \hat{\mathbf{S}}, \quad (4.21)$$

where $\hat{\mathbf{L}} = \vec{r} \times \vec{p}$, $\vec{\mu} = \frac{e}{m_e c} \hat{\mathbf{S}}$, and $f(r) = \frac{e}{2m_e^2 c^2 r} \frac{d\phi(r)}{dr}$. We can see that the interaction Hamiltonian takes the form of a spin-orbit interaction $\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}$.

For the one-electron atom without the effect of induced magnetic field, we have a hydrogen-like Hamiltonian

$$\hat{H}_0 = \frac{\hat{\mathbf{p}}^2}{2m_e} + V(r) = \frac{\hat{p}_r^2}{2m_e} + \frac{\hat{\mathbf{L}}^2}{2m_e r^2} + V(r), \quad (4.22)$$

with solutions $|nl\rangle$, when expressed in spatial coordinates, gives the wavefunction $\langle r|nl\rangle = \varphi(\vec{r}) = R_{nl}(r)Y_l^m(\theta, \varphi)$. When the effect of the induced magnetic field is considered as a perturbation to this Hamiltonian,

$$\hat{H} = \hat{H}_0 + \hat{H}' = \frac{\hat{p}_r^2}{2m_e} + \frac{\hat{\mathbf{L}}^2}{2m_e r^2} + V(r) = \frac{1}{2}f(r)(\hat{\mathbf{J}}^2 - \hat{\mathbf{L}}^2 - \hat{\mathbf{S}}^2), \quad (4.23)$$

where we used the relationship given by Eq. 4.16.

Using the solutions of the hydrogen (-like) atom solution, we get the equation

$$\hat{H}|nl\rangle = \left(E_n + \frac{\hbar^2}{2}f(r)[j(j+1) - l(l+1) - s(s+1)] \right) |nl\rangle = E|nl\rangle. \quad (4.24)$$

It is important to note that $|nl\rangle$ are not eigenstates of the full Hamiltonian \hat{H} , since $f(r)$ still depends on the radial coordinate r . However, we can apply the concept of expansion (perturbation theory) if the expectation value of $\langle f(r) \rangle$ of $f(r)$ is very small. We consider the expectation value of the energy for a state characterized by the quantum numbers $|nls\rangle$, or equivalently, $|nlj\rangle$, given by

$$E_{nlj} = \langle nlj|\hat{H}|nlj\rangle = E_n + \frac{\hbar^2}{2}[j(j+1) - l(l+1) - s(s+1)]\langle f(r) \rangle_{nl}, \quad (4.25)$$

since $f(r)$ does not depend on the spin degree of freedom s . Given j is either $l + \frac{1}{2}$ or $l - \frac{1}{2}$, we find that

$$j(j+1) - l(l+1) - s(s+1) = (l \pm \frac{1}{2})(l+1 \pm \frac{1}{2}) - l(l+1) - \frac{3}{4} = \pm(l + \frac{1}{2}) - \frac{1}{2}. \quad (4.26)$$

So, to first order in $\langle f(r) \rangle_{nl}$, the two energy levels become

$$E_{nlj}^+ \equiv E_{j=l+1/2} = E_n + \frac{\hbar^2}{2}l\langle f(r) \rangle_{nl} \quad (4.27)$$

$$E_{nlj}^- \equiv E_{j=l-1/2} = E_n - \frac{\hbar^2}{2}(l+1)\langle f(r) \rangle_{nl}. \quad (4.28)$$

To estimate the value of $\langle f(r) \rangle_{nl}$, we realize that the central potential is given by $V(r) = -Ze^2/r$, and that

$$f(r) = \frac{1}{2m_e^2 c^2 r} \frac{d}{dr} \left(-\frac{Ze^2}{r} \right) = \frac{Ze^2}{2m_e^2 c^2} \frac{1}{r^3}. \quad (4.29)$$

The expectation value of this function is given by

$$\langle f(r) \rangle = \frac{Ze^2}{2m_e^2 c^2} \int_0^\infty \frac{|R_{nl}(r)|^2}{r^3} r^2 dr = \frac{Ze^2}{2m_e^2 c^2} \frac{2}{a_0^3 n^3 l(l+1)(2l+1)}. \quad (4.30)$$

The ratio of the correction term $\hbar^2 \langle f(r) \rangle_{nl}$ to the atomic energy is given by

$$\frac{\hbar^2 \langle f(r) \rangle}{|E|} = \frac{(Z\alpha)^2}{n} \frac{1}{l(l+1/2)(l+1)}, \quad (4.31)$$

where $\alpha \equiv e^2/(4\pi\epsilon_0\hbar c) = 1/(137.037) = 7.297 \times 10^{-3}$ is called the *fine structure constant*. For a singly-charged atom ($Z = 1$), we confirm that this correction is indeed very small, on the order of $\sim \alpha^2$. The atomic energy levels corresponding to $l \geq 1$ are split into two due to spin-orbit coupling, where the energy level corresponding to $j = l + \frac{1}{2}$ increases by a fraction $\frac{1}{(2L+1)(l+1)} \frac{(Z\alpha)^2}{n}$, and the other level corresponding to $j = l - \frac{1}{2}$ decreases by a fraction $\frac{1}{l(2L+1)} \frac{(Z\alpha)^2}{n}$.

4.2.3 Spin-orbit coupling: relativistic correction

When relativistic effects are considered, the kinetic portion of the Hamiltonian should be represented as

$$\hat{H} = (\hat{p}^2 c^2 + m_e^2 c^4)^{1/2} - m_e c^2 + V(r) \simeq \frac{\hat{p}^2}{2m_e} - \frac{\hat{p}^4}{8m_e^3 c^2} + \dots + V(r), \quad (4.32)$$

for $|p| \ll mc$. When the second term in the expansion is treated as a small perturbation $\hat{H}' = \hat{p}^4/(8m_e^3 c^2)$, the correction term in the energy can be estimated using the eigenstates of the bare hydrogen atom solutions as

$$\langle nl | \hat{H}' | nl \rangle = -\frac{1}{8m_e^3 c^2} \langle \hat{p}^4 \rangle_{nl}. \quad (4.33)$$

Noting that

$$\hat{p}^2 |nl\rangle = 2m_e(E_n - V)|nl\rangle, \quad (4.34)$$

we can evaluate

$$\langle nl | \hat{p}^4 | nl \rangle = 4m_e^2 \langle nl | (E_n - V)^2 | nl \rangle. \quad (4.35)$$

Noting that $\langle 1/r \rangle = 1/(a_0 n^2)$ and $\langle 1/r^2 \rangle = 2/[(2l+1)a_0^2 n^3]$, and therefore $\langle nl | V | nl \rangle = -Ze^2/(a_0 n^2)$ and $\langle nl | V^2 | nl \rangle = 2(Ze^2)^2/[(2l+1)a_0^2 n^3]$, we can evaluate the correction term using the condition $E_n = m(Ze^2)^2/(2\hbar^2 n^2)$ as

$$\langle nl | \hat{H}' | nl \rangle = -|E_n| \frac{(Z\alpha)^2}{4n^2} \left[\frac{8n}{2l+1} - 3 \right] \quad (4.36)$$

Therefore, the fractional correction energy for the two fine-structure split energy levels are $(\frac{Z\alpha}{2n})^2 [\frac{4n}{l+1} - 3]$ and $(\frac{Z\alpha}{2n})^2 [\frac{4n}{l} - 3]$, respectively.

4.2.4 Spin-orbit coupling: Darwin term

In the Schrödinger equation, we have considered the electron to be a point particle such that the interaction between the electron and the Coulomb field of the nucleus is local. The first order correction to this assumption is that the electron's interaction with the Coulomb field has a non-local nature over a finite length scale, corresponding to the Compton wavelength of the electron, given by $\hbar/m_e c$. This correction term is expressed in the Hamiltonian as

$$\hat{H}_D = \frac{\hbar^2}{8m_e^2 c^2} \nabla^2 V(R). \quad (4.37)$$

Noting that $\nabla^2(1/r) = -4\pi\delta(\vec{r})$, we find that

$$\hat{H}_D = \frac{\pi e^2 \hbar^2}{2m_e^2 c^2} \delta(\vec{r}). \quad (4.38)$$

When we take the average of this potential over the electron wavefunction, we get

$$\langle \hat{H}_D \rangle = \frac{\pi e^2 \hbar^2}{2m_e^2 c^2} |\psi(\vec{0})|^2, \quad (4.39)$$

where $\psi(\vec{0})$ is the value of the wavefunction at the origin. Therefore the Darwin term only affects the s electrons with non-zero wavefunction value at the origin. Given that the s electrons are spread out over a length scale of Bohr radius a_0 , we find that

$$|\psi(\vec{0})|^2 \simeq \frac{1}{a_0^3} = \frac{m_e^3 e^6}{\hbar^6}. \quad (4.40)$$

This leads to the estimate of the Darwin term as

$$\langle \hat{H}_D \rangle \simeq m_e c^2 \frac{e^8}{\hbar^4 c^4} = m_e c^2 \alpha^4, \quad (4.41)$$

and

$$\langle \hat{H}_D \rangle / \langle \hat{H}_0 \rangle \simeq \frac{m_e c^2 \alpha^4}{m_e c^2 \alpha^2} = \alpha^2. \quad (4.42)$$