And again, we can define
\[ S^2 = S_x^2 + S_y^2 + S_z^2 \]  \hfill (2.354)
And same as above, \( [S^2, S_z] = 0 \), so we can measure \( S^2 \) and \( S_z \) at the same time.
\[ S^2 \left| s, m \right\rangle = s(s+1) \hbar^2 \left| s, m \right\rangle \]  \hfill (2.355)
\[ S_z \left| s, m \right\rangle = m \hbar \left| s, m \right\rangle \]  \hfill (2.356)
where \( s \) is a non-negative integer or half-integer, \( s = 0, 1/2, 1, 3/2, \ldots \). Once \( s \) is determined, \( m = -s, -s+1, \ldots, s-1, s \). For electrons, \( s = 1/2 \), and thus \( m = -1/2 \) or \( +1/2 \).

In addition, we know that \( \vec{S} \) and \( \vec{L} \) commute with each other,
\[ \left[ \vec{S}, \vec{L} \right] = 0 \]  \hfill (2.357)

Without spin-orbit coupling (i.e. the unperturbed Hamiltonian \( H_0 \)), we can easily prove that \( [H_0, \vec{S}] = [H_0, \vec{L}] = 0 \), as a result, we find that the following operators commute with one another, \( H_0, L_z, L_z, S_x, S_z \). So we can request our quantum states to be common eigenstates of all these operators: \( \left| n, l, m, s, s_z \right\rangle \)
\[ H_0 \left| n, l, m, s, s_z \right\rangle = -\frac{13.6 \text{ eV}}{n^2} \left| n, l, m, s, s_z \right\rangle \]  \hfill (2.358)
\[ L_z \left| E_n, l, m, s, s_z \right\rangle = l(l+1) \hbar^2 \left| n, l, m, s, s_z \right\rangle \]  \hfill (2.359)
\[ L_z \left| E_n, l, m, s, s_z \right\rangle = m \hbar \left| n, l, m, s, s_z \right\rangle \]  \hfill (2.360)
\[ S^2 \left| E_n, l, m, s, s_z \right\rangle = \frac{3}{4} \hbar^2 \left| n, l, m, s, s_z \right\rangle \]  \hfill (2.361)
\[ S_z \left| E_n, l, m, s, s_z \right\rangle = s \hbar \left| n, l, m, s, s_z \right\rangle \]  \hfill (2.362)

where \( s_z = +1/2 \) or \(-1/2 \). For an electron, we know that \( s \) is always \( 1/2 \), so we don’t really need to write it out: \( \left| n, l, m, s_z \right\rangle \). Compare to the results without spins (\( \psi_{\text{no spin}} \)), the only thing we get here is an extra index \( s_z = \pm 1/2 \). This quantum number tells me whether my spin is pointing up or down. At the end of the day, we didn’t get anything beyond what we have already known, except that now we need to specify whether the spin of the electron is up or down.

With SO coupling, the basis described above is NOT a good option, because \( \left( n, l, m, s_z \right| H_{\text{SO}} \right| n', l', m', s_z' \rangle \neq 0 \), i.e. to do degenerate perturbation theory, we will need a new basis.

**Basis with \( H_{\text{SO}} \)**

To get the proper basis, we can go throw the derivation that we demonstrated for degenerate perturbation theory. Here, instead, we will use a trick to get the correct basis direction. The trick is what we proved early on. We know that if we can find a quantum operator, \( \hat{A} \), which commutes with both \( H_0 \) and the perturbation \( H_{\text{SO}} \), we can use common eigenstates of \( \hat{A} \) and \( H_0 \) as a set of basis. If in this set, every state has a different eigenvalue for \( \hat{A} \), then it is a good state for degenerate perturbation theory.

In the previous section (restitisptic correction), we used \( L^2 \) and \( L_z \) to serve as the \( \hat{A} \) operator. Here, after taking into account spins and for the perturbation \( H_{\text{SO}} \), we will need to use \( L^2, S^2, \hat{P} \) and \( J_z \) as \( \hat{A} \).

If an electron have both orbit and spin angular momenta, we can add them up to get the total angular momentum
\[ \vec{J} = \vec{L} + \vec{S} \]  \hfill (2.363)
or equivalently,
\[ J_x = L_x + S_x \]  \hfill (2.364)
\[ J_y = L_y + S_y \]  \hfill (2.365)
\[ J_z = L_z + S_z \]  \hfill (2.366)
For $J_s$, we have the same commutation relation
\[ [J_\ell, J_s] = i \hbar J_z \]  
\[ [J_y, J_z] = i \hbar J_x \]  
\[ [J_\ell, J_y] = i \hbar J_\ell \]

And we can also define $J^2$ as
\[ J^2 = J_\ell^2 + J_s^2 + J_z^2 \]

Same as $L$ and $S$, we know that $[J^2, J_\ell] = 0$. So we can measure $J^2$ and $J_\ell$ at the same time
\[ J^2 | j, m \rangle = j(j + 1) \hbar^2 | s, m \rangle \]
\[ J_\ell | j, m \rangle = m \hbar | s, m \rangle \]

where $j$ is an integer or half-integer, $j = 0, 1/2, 1, 3/2, \ldots$ Once $j$ is determined, $m = -j, -j+1, \ldots, j-1, j$. For electrons, $s = 1/2$, and thus $m = -1/2$ or +1/2.

If we have a particle with spin quantum number $s$ and orbit angular momentum quantum number $l$, then $j = l + s$, $l + s - 1, \ldots | l - s |$. NOTE: $j$ cannot be negative. For spin $s = 1/2$, this means that $j = l - 1/2$ or $j = l + 1/2$ for $l \geq 1$. And $j = 1/2$ if $l = 0$.

- If we put an electron on an s-wave state ($l = 0$), the total angular momentum $j = 1/2$
- If we put an electron on an p-wave state ($l = 1$), the total angular momentum $j = 1/2$ or 3/2
- If we put an electron on an d-wave state ($l = 2$), the total angular momentum $j = 3/2$ or 5/2
- If we put an electron on an f-wave state ($l = 3$), the total angular momentum $j = 5/2$ or 7/2
- ...

In our homework, we will show that $J^2, J_\ell, L^2, S^2$ compute with $H_{SO}$. It is also straightforward to see that $J^2, J_\ell, L^2, S^2$ all commute with $H_0$, so we can use them as our $\hat{A}$ operator. In addition, it is also easy to verify that these four operators commute with each other, so we can define common eigenstates for $H_0, J^2, J_\ell, L^2, S^2$ and using this common eigenstates as our basis for perturbation theory

\[ H_0 | n, l, s, j, j_z \rangle = -\frac{13.6 \text{ eV}}{\hbar^2} | n, l, s, j, j_z \rangle \]
\[ L^2 | n, l, s, j, j_z \rangle = l(l + 1) \hbar^2 | n, l, s, j, j_z \rangle \]
\[ S^2 | n, l, s, j, j_z \rangle = s(s + 1) \hbar^2 | n, l, s, j, j_z \rangle = \frac{3}{4} \hbar^2 | n, l, s, j, j_z \rangle \]
\[ J^2 | n, l, s, j, j_z \rangle = j(j + 1) \hbar^2 | n, l, s, j, j_z \rangle \]
\[ J_\ell | n, l, s, j, j_z \rangle = j \hbar | n, l, s, j, j_z \rangle \]

Notice that
\[ J^2 = \vec{J} \cdot \vec{J} = (\vec{L} + \vec{S}) \cdot (\vec{L} + \vec{S}) = L^2 + S^2 + 2 \vec{L} \cdot \vec{S} \]

As a result,
\[ \vec{S} \cdot \vec{L} = \frac{J^2 - L^2 - S^2}{2} \]

So we can write our perturbation as
\[ H_{SO} = \frac{e^2}{8 \pi \epsilon_0} \frac{1}{m^2 c^2 r^3} \vec{S} \cdot \vec{L} = \frac{e^2}{8 \pi \epsilon_0} \frac{1}{m^2 c^2 r^3} \frac{J^2 - L^2 - S^2}{2} \]

The first order perturbation theory
\[ E_{n, l, s, j, j_z}^{1} = \langle n, l, s, j, j_z | H_{SO} | n, l, s, j, j_z \rangle = \frac{e^2}{8 \pi \epsilon_0} \frac{1}{2 m^2 c^2} \langle n, l, s, j, j_z | J^2 - L^2 - S^2 \rangle \frac{J^2 - L^2 - S^2}{r^3} | n, l, s, j, j_z \rangle \]
\[ \frac{e^2}{8 \pi \varepsilon_0 \frac{1}{2 m^2 c^2}} \begin{pmatrix} n, l, s, j, j_z \end{pmatrix} \left( \frac{j(j+1) - l(l+1) - s(s+1)}{r^3} \right) \frac{1}{n, l, s, j, j_z} = \]

\[ \frac{e^2 \hbar^2}{16 \pi \varepsilon_0} \left( \frac{j(j+1) - l(l+1) - s(s+1)}{r^2} \right) \frac{1}{n, l, s, j, j_z} = \]

The average value for \( \frac{1}{r^3} \) is known for the unperturbed Hamiltonian

\[ \begin{pmatrix} n, l, s, j, j_z \end{pmatrix} \left( \frac{1}{r^3} \right) \begin{pmatrix} n, l, s, j, j_z \end{pmatrix} = \int d^3 r \psi_{n,l,m}(r, \theta, \phi) \frac{1}{r^3} \psi_{n,l,m}(r, \theta, \phi) = \frac{1}{n(l+1/2)(l+1)n^3 a^3} \]  

(2.382)

So

\[ E_{n,l,m,j} = \frac{\hbar^2}{16 \pi \varepsilon_0} \left( \frac{j(j+1) - l(l+1) - s(s+1)}{m^2 a^2} \right) \frac{1}{n, l, s, j, j_z} = \]

\[ \frac{e^2 \hbar^2}{16 \pi \varepsilon_0} \left( \frac{j(j+1) - l(l+1) - \frac{3}{4}}{m^2 a^2} \right) \frac{1}{n, l, s, j, j_z} = \]

(2.383)

Recall that in the previous section, we find that the relativistic correction is (at the first order)

\[ E_{rel} = -\frac{e^2}{n^2} \left( \frac{\varepsilon_0}{8 \pi \varepsilon_0 a} \right) \]

(2.385)

\[ E_{n,l,m,j} = \frac{e^2 \hbar^2}{16 \pi \varepsilon_0} \left( \frac{j(j+1) - l(l+1) - s(s+1)}{m^2 a^2} \right) \frac{1}{n, l, s, j, j_z} = \]

\[ \frac{e^2 \hbar^2}{16 \pi \varepsilon_0} \left( \frac{j(j+1) - l(l+1) - \frac{3}{4}}{m^2 a^2} \right) \frac{1}{n, l, s, j, j_z} = \]

(2.386)

Recall that in the previous section, we find that the relativistic correction is (at the first order)

\[ \frac{(E_n^0)^2}{2 m^2} \left( \frac{4 n}{l + \frac{3}{2}} \right) - 3 \]

(2.387)

If we combine both effects together, to the first order, the energy is

\[ E_{n,l,m,j} = E_n^0 + \frac{(E_n^0)^2}{2 m^2} \left( \frac{2(j+1) - l(l+1) - \frac{3}{4}}{n} \right) \frac{4 n}{l + \frac{3}{2}} + 3 \]

(2.388)

Notice that \( j = l + 1/2 \) or \( l = -1/2 \), so we have \( l = j - 1/2 \) or \( j + 1/2 \). For \( l = j - 1/2 \), we find that

\[ E_{n,l,m,j} = E_n^0 - \frac{(E_n^0)^2}{2 m^2} \left( \frac{4 n}{j + 1/2} - 3 \right) \]

(2.389)

for \( l = j + 1/2 \), we find exactly the same result

\[ E_{n,l,m,j} = E_n^0 - \frac{(E_n^0)^2}{2 m^2} \left( \frac{4 n}{j + 1/2} - 3 \right) \]

(2.390)

So we conclude, no matter what, we have
After taking into account both SO coupling and relativistic correction, we find that the energy of a quantum state only depends on \( n \) and \( j \),

\[
E_{n,j,j_z} = E_n^0 - \frac{(E_n^0)^2}{2mc^2} \left( \frac{4n}{j+1/2} - 3 \right) + \ldots
\]

(2.391)

This is the fine structure correction in a hydrogen atom.

According to this formula, the fine structure correction always reduces the energy of a state by a very small fraction (the correction is \( \alpha^2 \sim 10^{-4} \), which is a 0.01% change). The smaller the \( j \) is the bigger this correction is. So s-wave states (with \( l = 0 \) get the largest modification). For states with \( l > 0 \), e.g. p-wave, d-wave, etc., they splits into two different energy levels (with \( j = l - 1/2 \) and \( j = l + 1/2 \), and the former has lower energy than the latter).

NOTE: the fine structure correction can also be written as

\[
E_{n,j} = E_n^0 \left[ 1 - \frac{E_n^0}{2mc^2} \left( \frac{4n}{j+1/2} - 3 \right) + \ldots \right]
\]

(2.393)

because

\[
E_n^0 = -\frac{1}{2n^2} mc^2 \left( \frac{e^2}{4\pi\epsilon_0\hbar c} \right)^2 = -\frac{\alpha^2}{2n^2} mc^2
\]

(2.394)

where \( \alpha \) is the fine structure constant

\[
\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} \approx \frac{1}{137.036}
\]

(2.395)

we can rewrite the formula as

\[
E_{n,j} = E_n^0 \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{4n}{j+1/2} - 3 \right) + \ldots \right] = E_n^0 \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+1/2} - \frac{3}{4} \right) + \ldots \right] = -\frac{13.6\text{ eV}}{n^2} \left[ 1 + \frac{\alpha^2}{n^2} \left( \frac{n}{j+1/2} - \frac{3}{4} \right) + \ldots \right]
\]

(2.396)

### 2.6. The Zeeman effect

In the previous section, we found that after considering relativistic effects (i.e., fine structure), the eigenenergies in a hydrogen atom only depends on the quantum numbers \( n \) and \( j \). In particular, the energy is independent of \( j_z \).

**For a fixed \( j, j_z = -j, -j + 1, \ldots, j - 1, j \), all have the same energy, i.e. 2 \( j + 1 \)-fold degeneracy.**

In this section, we will show that in the presence of an external \( B \) field, these 2 \( j + 1 \)-fold degeneracy will be lifted.

In a magnetic field, the energy of a magnetic dipole is \( E = -\vec{\mu} \cdot \vec{B} \). So for an atom

\[
H_B = - (\vec{\mu}_L + \vec{\mu}_S) \cdot \vec{B}
\]

(2.397)

where \( \vec{\mu}_L \) is the magnetic dipole moment from orbit motion

\[
\vec{\mu}_L = -\frac{e}{2m} \vec{L} = -\mu_B \frac{\vec{L}}{\hbar}
\]

(2.398)

and \( \vec{\mu}_S \) is the magnetic dipole moment from electron spin

\[
\vec{\mu}_S = -2\times \frac{e}{2m} \vec{S} = -\frac{e}{m} \vec{S} = -2\mu_B \frac{\vec{S}}{\hbar}
\]

(2.399)

where \( \mu_B = \frac{eh}{2m} = 5.788 \times 10^{-5} \text{ eV/T} \) is Bohr magneton. Here, \( \vec{L} \) and \( \vec{S} \) are angular momenta from orbit motion and electron spin respectively.