\[ H_2' = \mu_B \frac{\vec{L} + 2 \vec{S}}{\hbar} \cdot \vec{B} \]  

(2.400)

Without loss of genericity, we will set \( B \) to be along the \( z \) direction, so the total energy is

\[ \vec{B} = B \hat{z} \]  

(2.401)

As a result,

\[ H_2' = \mu_B B \frac{L_z + S_z}{\hbar} \]  

(2.402)

Consider

\[ H = H_0 + H_2' + H_{SO}' + H_z' \]  

(2.403)

where \( H_0 \) is the Hamiltonian that we studied in QM I (kinetic energy + 1/r attraction), and \( H_z' \) is the relativistic correction. \( H_{SO}' \) is the SO coupling effect, and \( H_2' = \mu_B B \frac{L_z + S_z}{\hbar} \).

### 2.6.1. Difficulty

For the Hamiltonian above \( H \), the key difficulty lies in the fact that the last two terms, \( H_{SO}' \) and \( H_z' \), do not commute with each other. For \( H_2' \), we must know \( L_z \) and \( S_z \). However, we have learned early on \( H_{SO}' \) doesn’t commute with \( L_z \) and \( S_z \) (\( H_{SO}' \) commutes with \( j_z \), but not with \( S_z \) or \( L_z \), as we showed in our homework). So, we cannot measure \( H_{SO}' \) with \( L_z \) and \( S_z \) at the same time, but \( H_2' \) needs information about \( L_z \) and \( S_z \). This is the confliction.

**NOTE:** this problem comes from the g factor for electrons. \( \mu_\ell = -\mu_B \frac{\vec{L}}{\hbar} \) and \( \mu_S = -2 \mu_B \frac{\vec{S}}{\hbar} \), the prefactor for them are DIFFERENT! (differ by a factor of 2, i.e., the g-factor). If there is no this extra factor \( g = 2 \), things would be very easy. There, \( H_2' = \mu_B B \frac{L_z + S_z}{\hbar} = \mu_B B \frac{j_z}{\hbar} \), so we only need \( J_j \). But unfortunately, \( H_2' \) is not proportional to \( J_j \).

### 2.6.2. Strong field

When \( H_z' \gg H_{SO}' \), we can treat \( H_{SO}' \) and \( H_z' \) (they two are comparable as we learned in the previous section) as perturbation, and thus our unperturbed Hamiltonian is

\[ H_0 + H_z' \]  

(2.404)

The eigenstates of this Hamiltonian is the same as the eigenstates of \( H_0 \): \( |n, l, m_l, m_s\rangle \). Here, \( |n, l, m_s\rangle \) are the eigenfunctions that we learned in QM I. Here, we add back the spin \( S_z \) quantum state \( m_s \)

\[ L_z |n, l, m_l, m_s\rangle = \hbar (l + 1) |n, l, m_l, m_s\rangle \]  

(2.405)

\[ S_z |n, l, m_l, m_s\rangle = m_s \hbar |n, l, m_l, m_s\rangle \]  

(2.406)

\[ L_z |n, l, m_l, m_s\rangle = m_l \hbar |n, l, m_l, m_s\rangle \]  

(2.407)

\[ H_0 |n, l, m_l, m_s\rangle = -\frac{13.6 \text{ eV}}{n^2} |n, l, m_l, m_s\rangle \]  

(2.408)

\[ H_z' |n, l, m_l, m_s\rangle = \frac{\mu_B B}{\hbar} (L_z + 2 S_z) |n, l, m_l, m_s\rangle = \frac{\mu_B B}{\hbar} L_z |n, l, m_l, m_s\rangle + 2 \frac{\mu_B B}{\hbar} S_z |n, l, m_l, m_s\rangle = \frac{\mu_B B}{\hbar} \hbar m_l |n, l, m_l, m_s\rangle + \frac{\mu_B B}{\hbar} \hbar m_s |n, l, m_l, m_s\rangle \]  

(2.409)

So our zeroth order eigenenergy is

\[ E_{n,l,m_l,m_s} = -\frac{13.6 \text{ eV}}{n^2} + \mu_B B (m_l + 2 m_s) \]  

(2.410)

At \( B = 0 \), we know that energy is independent of \( m_l \) and \( m_s \), i.e., all quantum states are degenerate with (at least \( 2(2l+1) \))-fold degenerate. For finite \( B \) however, these states splits.
Example: if we consider states \( n = 2 \) and \( l = 1 \) (first excited states with orbit angular moment quantum number \( l = 1 \)). There, \( m_l = -1, 0, +1 \) and \( m_s = \frac{-1}{2} \) or \( \frac{+1}{2} \). At \( B = 0 \), all these six states are degenerate \( (E = -13.6/4 = -3.4 \text{ eV}) \). In the presence of strong \( B \) field, 

\[
E_{\mu, l, m_s, m_l}^0 = \begin{cases}
-3.4 eV + 2 \mu_B B & m_l = +1 \text{ and } m_s = +1/2 \\
-3.4 eV + \mu_B B & m_l = 0 \text{ and } m_s = +1/2 \\
-3.4 eV & m_l = -1 \text{ and } m_s = +1/2 \text{, or } m_l = +1 \text{ and } m_s = -1/2 \\
-3.4 eV - \mu_B B & m_l = 0 \text{ and } m_s = -1/2 \\
-3.4 eV - 2 \mu_B B & m_l = -1 \text{ and } m_s = -1/2 \\
\end{cases}
\]

(2.411)

Now, we consider \( H_{SO}^* \) and \( H_r^* \). Because we assumed that they are much smaller than \( H_0 \) and \( H_r \), we treat them as perturbation and compute the first order correction to the eigenenergy 

\[
E_{\mu, l, m_s, m_l}^1 = \langle n, l, m_l, m_s \mid H_r^* + H_{SO}^* \mid n, l, m_l, m_s \rangle
\]

(2.412)

The realistic correction is same as what we learned before 

\[
\langle n, l, m_l, m_s \mid H_r^* \mid n, l, m_l, m_s \rangle = -\frac{(E_n^0)^2}{2m c^2} \left( \frac{4n}{l+\frac{1}{2}} - 3 \right)
\]

(2.413)

Because 

\[
E_n^0 = -\frac{1}{2 n^2} \frac{m}{\hbar^2} \left( \frac{e^2}{4 \pi \epsilon_0} \right)^2 = -\frac{13.6}{n^2} \text{ eV}
\]

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

we know that 

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

(2.416)

so 

\[
\langle n, l, m_l, m_s \mid H_r^* \mid n, l, m_l, m_s \rangle = -\frac{E_n^0}{2mc^2} \left( \frac{4n}{l+\frac{1}{2}} - 3 \right) = -\frac{E_n^0}{2mc^2} \frac{\alpha^2}{2 n^2} \left( \frac{4n}{l+\frac{1}{2}} - 3 \right) = -13.6 \text{ eV} \frac{\alpha^2}{n^2} \left( \frac{n}{l+\frac{1}{2}} - \frac{3}{4} \right)
\]

(2.417)

For spin-orbit coupling, 

\[
\langle n, l, m_l, m_s \mid H_{SO}^* \mid n, l, m_l, m_s \rangle = \langle n, l, m_l, m_s \mid \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \mid n, l, m_l, m_s \rangle = \frac{e^2}{8 \pi \epsilon_0} \frac{1}{m^2 c^2 r^3} \langle n, l, m_l, m_s \mid \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \mid n, l, m_l, m_s \rangle
\]

(2.418)

Notice that in the zeroth order wavefunctions, \( \mid n, l, m_l, m_s \rangle \), spin and orbit angular momenta are independent of each other, so 

\[
\langle n, l, m_l, m_s \mid \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \mid n, l, m_l, m_s \rangle = \langle \hat{\mathbf{S}} \rangle \langle \hat{\mathbf{L}} \rangle = \langle S_x \rangle \langle L_x \rangle + \langle S_y \rangle \langle L_y \rangle + \langle S_z \rangle \langle L_z \rangle
\]

(2.419)

In QM I, we learned that for eigenstates of \( L^2 \) and \( L_z \), \( \langle L_x \rangle = \langle L_y \rangle = 0 \). And similarly, \( \langle S_x \rangle = \langle S_y \rangle = 0 \). And thus 

\[
\langle n, l, m_l, m_s \mid \hat{\mathbf{S}} \cdot \hat{\mathbf{L}} \mid n, l, m_l, m_s \rangle = \langle \hat{\mathbf{S}} \rangle \langle \hat{\mathbf{L}} \rangle = \langle S_z \rangle \langle L_z \rangle = m_s \hbar m = m_s \hbar
\]

(2.420)

As a result, 

\[
\langle n, l, m_l, m_s \mid H_{SO}^* \mid n, l, m_l, m_s \rangle = \frac{e^2}{8 \pi \epsilon_0} \frac{1}{m^2 c^2} \left( \frac{m_s m_l \hbar}{r^3} \right) = \frac{e^2}{8 \pi \epsilon_0} \frac{1}{m^2 c^2} \left( \frac{m_l m_s \hbar}{r} \right)
\]

(2.421)

and 

\[
\langle n, l, s, j_z \mid \mathbf{r} \frac{1}{r^3} \mid n, l, m_l, m_s \rangle = \int d^3r \psi_{n,m_l,m_s}(r, \theta, \phi) \frac{1}{r^3} \psi_{n,m_l,m_s}(r, \theta, \phi) = \frac{1}{l(l+1/2)(l+1)n^3 \alpha^3}
\]

(2.422)
where $a$ is the Bohr radius $a = \frac{\hbar^2}{m c^2}\\$

So

$$\langle n, l, m_s, m_l | H_{SO} | n, l, m_s, m_l \rangle = \frac{e^2}{8 \pi \epsilon_0} \frac{m_s m_l}{m^2 c^2} \frac{1}{(\hbar c)^3} \frac{1}{l(l+1/2)(l+1)n^3}$$

$$= \frac{1}{2} \frac{e^2}{4 \pi \epsilon_0} c \frac{m_s m_l}{\hbar^2} l(l+1/2)(l+1)n^3$$

$$= \frac{1}{2} \frac{e^2}{4 \pi \epsilon_0} c \frac{m_s m_l}{\hbar^2} l(l+1/2)(l+1)n^3$$

(2.423)

Because

$$E_n^0 = -\frac{1}{2} \frac{m}{\hbar^2} \frac{e^2}{4 \pi \epsilon_0} = -\frac{13.6 eV}{n^2}$$

$$\alpha = \frac{\hbar^2}{4 \pi \epsilon_0 h c} = \frac{1}{137.036}$$

(2.424)

we can rewrite the formula as

$$\langle n, l, m_s, m_l | H_{SO} | n, l, m_s, m_l \rangle = 13.6 \text{ eV } \alpha^2 \frac{m_s m_l}{l(l+1/2)(l+1)n^3}$$

(2.425)

So our first order correction is

$$E_{n,l,m_s,m_l} = \langle n, l, m_s, m_l | H'_{SO} | n, l, m_s, m_l \rangle = -13.6 \text{ eV } \alpha^2 \frac{m_s m_l}{l(l+1/2)(l+1)n^3}$$

$$+ 13.6 \text{ eV } \alpha^2 \frac{m_s m_l}{l(l+1/2)(l+1)n^3}$$

$$= \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left( \frac{3}{4 n} - \frac{1}{l(l+1/2)(l+1)} \right)$$

(2.426)

So

$$E_{n,l,m_s,m_l} = E_{n,l,m_s,m_l}^0 + E_{n,l,m_s,m_l}$$

$$= -13.6 \text{ eV } \alpha^2 \frac{m_s m_l}{l(l+1/2)(l+1)n^3}$$

$$+ 13.6 \text{ eV } \alpha^2 \frac{m_s m_l}{l(l+1/2)(l+1)n^3}$$

$$= \frac{13.6 \text{ eV}}{n^3} \alpha^2 \left( \frac{3}{4 n} - \frac{1}{l(l+1/2)(l+1)} \right)$$

(2.427)

Bottom line: at very strong field (second term much larger than the last one), the energy splittings between the levels are proportional to $B$ and the slope is proportional to $\mu_B(m + 2 m_3)$. The eigenstates are (almost) $| n, l, m_s, m_l \rangle$, where $m_s$ and $m_l$ are good quantum numbers. (we should arrange the states according to the orbit and spin angular moment, NOT the total angular momentum $j$).

2.6.3. Weak field

When $H_z \ll H_{SO}$, we can treat $H'_{SO}$ as a small perturbation. The zeroth order Hamiltonian (i.e. ignoring $H_{SO}$) is what we studied in the previous section. There, we know that eigenstates are $| n, j, l, s, m_j \rangle$ and the eigenenergy is

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

(2.428)

In first order perturbation theory, the energy correction is

$$E_{n,j,l,s,m_j} = \langle n, j, l, s, m_j | H'_{SO} | n, j, l, s, m_j \rangle = \frac{\mu_B}{\hbar} \left( \frac{\hbar + 2 \vec{S}}{\hbar} \right) \left( \vec{B} \cdot \vec{L} + 2 \vec{B} \cdot \vec{S} \right) | n, j, l, s, m_j \rangle$$

(2.429)

The key is to compute expectation values of $\langle \vec{L} \rangle$ and $\langle \vec{S} \rangle$ for eigenstates of $J^2$ and $J_z$. Here, we use the fact that

$$\langle \vec{L} \rangle = \langle \vec{S} \rangle = 0$$

(2.430)

So

$$\langle \vec{L} \rangle = \langle \vec{S} \rangle = 0$$

(2.431)