Quantum Mechanics and Atomic Physics

Lecture 20:
Hydrogen Fine Structure / Spin-Orbit Coupling / Zeeman Effect

http://www.physics.rutgers.edu/ugrad/361

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Last time

- Hydrogen atom: electron in circular orbit
  - creates an *internal* magnetic field (moment) in an atom
  - electron spin creates a spin magnetic moment (*intrinsic* angular momentum).

- In an external B field, every Bohr model photon line should split into exactly 3 equally spaced lines:
  \[ \Delta E = g \mu_B B \text{ with } g = 1: \text{ Normal Zeeman Effect} \]

- In many atoms (including Hydrogen) splitting is not
  \[ \Delta E = 1 \mu_B B. \text{ In this case } g \neq 1. \text{ Zeeman effect is “anomalous”}. \]
  - Photon lines often split into more than 3 in an external B field
  - Even when B=0 there is a splitting of most energy levels in hydrogen and many other atoms!
Energy Level Diagrams

\[
B=0
\]

\[
B \neq 0
\]
Spin-Orbit Coupling

- The magnetic moments are:

\[ \vec{\mu}_L = -g \frac{e}{2m} \hat{L} \quad \text{with } g=1 \quad \text{(orbit)} \]

\[ \vec{\mu}_S = -g \frac{e}{2m} \hat{S} \quad \text{with } g=\alpha \quad \text{(spin)} \]

- Interaction of \( \mu_L \) and \( \mu_S \) causes a fine-structure splitting of energy levels, even if \( B_{\text{external}} = 0 \)!
Spin-Orbit Coupling, con’t

“Vector model” of angular momentum:

Total angular momentum is:

\[ \vec{J} = \vec{L} + \vec{s} \]

J precesses about the z-axis

\[ J = |\vec{J}| = \sqrt{j(j+1)} \hbar \]
\[ J_z = m_j \hbar \]

Now we have

Total angular momentum quantum number \( j \)

Total magnetic quantum number \( m_j \)

**Dirac Theory:** use \( n, \ell, j, m_j \)

Instead of: \( n, \ell, m_{\ell}, m_s \)
Hydrogen Fine-Structure

- Only one electron in Hydrogen so $s=1/2$

$$j = |l-s|, \ldots, (l+s)$$

- Most of the Schrodinger energy levels in Hydrogen should split into two levels

- Exception: for $\ell=0$, note $j=1/2$ only, so no splitting of $\ell=0$ states.
Hydrogen Fine-Structure, con’t

- Recall, the Bohr energy levels are:
  \[ E_{\text{Bohr}} = -13.6 \text{eV} \cdot \frac{1}{n^2} \]

- Recall, the fine-structure constant:
  \[ \alpha = \frac{e^2}{4 \pi \varepsilon_0 c} \approx \frac{1}{137} \]

- Now, in the Dirac theory:
  \[ E_{\text{Dirac}} = E_{\text{Bohr}} \left[ 1 + \frac{\alpha^2}{n} \left( \frac{1}{j+y_2} - \frac{3}{4n} \right) \right] \]

- In Schrödinger (and Bohr) theory, levels of the same \( n \) are degenerate.
- In the Dirac theory, levels of the same \( n \) and \( j \) are degenerate.
Spectroscopic Notation

- For each energy level:

\[ n^{2s+1}L_j \]

- Since \( s = \frac{1}{2} \) in Hydrogen, \( 2s + 1 = 2 \) always.

- Example:
  - \( n = 4, \ell = 1, j = \frac{3}{2} \)
  - We write this as \( 4^2P_{3/2} \)
  - Called “four doublet P three-halves”
Energy Level diagram revisited (again!)

Now in the Dirac theory with $B_{\text{external}} = 0$

Notes:

1. Clearly this is not to scale!
2. Levels of the same $n$ and $j$ are degenerate
3. S states ($\ell = 0$) are labeled “doublet” even though they are not!
Compare to Bohr/Shrodinger theory

\[ B_{\text{external}} = 0 \]
Example

- By how much does the $1^2S_{1/2}$ energy differ from the Bohr value of $-13.6$ eV?

\[
\Delta E_{F_8} = E_{Bohr} \left[ \frac{\alpha^2}{n} \left( \frac{1}{j+y_2} - \frac{3}{4n} \right) \right] = -13.6\text{eV} \left[ \left( \frac{1}{137} \right)^2 \left( \frac{1}{4} \right) \left( \frac{1}{y_2+y_2} - \frac{3}{4(1)} \right) \right] = -13.6\text{eV} \left( 1.33 \times 10^{-5} \right) = -1.81 \times 10^{-4} \text{eV}
\]

- A little **below** the Bohr value

- This is generally true
Example

Find the energy separation of $2\ 2P_{1/2}$ and $2\ 2P_{3/2}$

$$n=2: \quad E_{\text{Bohr}} = \frac{-13.6\text{eV}}{(2)^2} = -3.4\text{eV}$$

$$\Delta E_{FS}(j=\frac{1}{2}) = -(3.4\text{eV})\left(\frac{1}{137}\right)^2\left(\frac{1}{2}\right)\left(\frac{1}{2\pi r_{1\frac{1}{2}}} - \frac{3}{4.2}\right)$$

$$= -5.66 \times 10^{-5}\text{eV}$$

$$\Delta E_{FS}(j=\frac{3}{2}) = -(3.4\text{eV})\left(\frac{1}{137}\right)^2\left(\frac{1}{2}\right)\left(\frac{1}{2\pi r_{1\frac{3}{2}}} - \frac{3}{4.2}\right)$$

$$= -1.13 \times 10^{-5}\text{eV}$$

$$E(2P_{3/2}) - E(2P_{1/2}) = +4.53 \times 10^{-5}\text{eV}$$

This is why it’s called “fine” structure!
Selection Rules for radiative transitions

- Similar to before, we have these selection rules:

\[
\begin{align*}
\Delta l &= \pm 1 \\
\Delta j &= 0, \pm 1 \\
\Delta m_j &= 0, \pm 1
\end{align*}
\]

- So, for example:
  - Forbidden or allowed?
  - \(2 \, S_{1/2} \rightarrow 1 \, S_{1/2}\)
    - is forbidden
  - \(2 \, P_{3/2} \rightarrow 1 \, S_{1/2}\)
    - is allowed
  - \(2 \, P_{1/2} \rightarrow 1 \, S_{1/2}\)
    - is allowed
Anomalous Zeeman Effect

- Now we will again place the Hydrogen atom in an external B field

- Again, the magnetic moments are:

\[ \mathbf{\mu}_e = -g \frac{e}{2m} \mathbf{I} \quad \text{with } g = 1 \]
\[ \mathbf{\mu}_s = -g \frac{e}{2m} \mathbf{S} \quad \text{with } g = 2 \]

- Let’s draw all the vectors ....
- $\mu_L$ is antiparallel to $L$
- $\mu_S$ is antiparallel to $S$

$$\vec{\mu}_{\text{Tot}} = \vec{\mu}_L + \vec{\mu}_S = -\frac{e}{2m} (\vec{L} + 2\vec{S})$$

- $\mu_{\text{tot}}$ is not antiparallel to $J$
  - This is because $g \neq 1$ in formula for $\mu_S$
- So we cannot write
  $$\vec{\mu}_{\text{Tot}} = (\text{const}) \vec{J}$$

- Instead, we can define “the” magnetic moment as the component of $\mu_{\text{tot}}$ along the direction of $J$
- This is called $\mu_J$
The Magnetic Moment

So now we can define:

\[ M_J = \frac{\hat{\mu}_{\text{tor}} \cdot \hat{J}}{J} \]

\[ \hat{\mu}_{\text{tor}} = \hat{\mu}_L + \hat{\mu}_S = -\frac{e}{2m} (\hat{L} + 2\hat{S}) \]

\[ = -\frac{e}{2m} (\hat{S} + \hat{S}) \]

Since \( \hat{J} = \hat{L} + \hat{S} \)

\[ \Rightarrow M_J = -\frac{e}{2m} \left( \frac{\hat{J} \cdot \hat{J} + \hat{S} \cdot \hat{J}}{\sqrt{\hat{J} \cdot (j+1) \hat{t}}} \right) \]

Used \( \hat{J} = \sqrt{j(j+1) \hat{t}} \)

\[ \Rightarrow M_J = -\frac{e}{2m} \frac{1}{\sqrt{j(j+1) \hat{t}}} \left( j(j+1) \hat{t}^2 + i s(j+1) \sqrt{j(j+1) \hat{t}^2 \cos \theta} \right) \]

\[ M_J = -\frac{e \hat{t}}{2m} \left( \sqrt{j(j+1)} + \sqrt{s(j+1)} \cos \theta \right) \]

\( \theta \) is angle between \( S \) and \( J \)
Use the law of cosines

\[ L^2 = J^2 + S^2 - 2JS \cos \theta \]

\[ L (\ell + 1) h^2 = j (j+1) h^2 + s (s+1) h^2 - 2 \sqrt{j(j+1)} \sqrt{s(s+1)} h^2 \cos \theta \]

\[ \cos \theta = \frac{j(j+1) + s(s+1) - L(\ell+1)}{2 \sqrt{j(j+1)} \sqrt{s(s+1)}} \]

\[ \mu_J = -\frac{e \hbar}{2m} \left[ \sqrt{j(j+1)} + \frac{j(j+1) + s(s+1) - L(\ell+1)}{2 \sqrt{j(j+1)}} \right] \]

\[ \mu_J = -\frac{e \hbar}{2m} \sqrt{j(j+1)} \cdot \mathbf{g} \]

\[ g = 1 + \frac{j(j+1) + s(s+1) - L(\ell+1)}{2 j(j+1)} \]

This is called the Landé g-factor

This is “the” magnetic moment
Back to anomalous Zeeman effect

- If the atom is placed in an external B field, the energy levels will split:

\[
\Delta E = -\mathbf{\mu}_J \cdot \mathbf{B} = - (g \frac{e}{2m}) J \cdot \mathbf{B} = g \frac{e}{2m} B J \cos \theta = g \frac{e}{2m} B J \bar{\gamma} = g \frac{e}{2m} B m J h
\]

\[\Rightarrow \Delta E = m_J g \mu_B B \]

- Again \( \mu_B \) is the Bohr magneton
- And \( g \) is the Landé g-factor given earlier
Example

For $B=0$, $3 \, S_{1/2}$ and $3 \, P_{1/2}$ are degenerate because they have the same $n$ and $j$. What happens when $B \neq 0$?

- Since $j=1/2$, they split into $2j+1$ states, which in this case is 2 states
- With $m_j = -1/2$ and $m_j=+1/2$
- And energies:

$$E = E_{B=0} + m_j g \mu_B B$$
It should not be a surprise that $g=2$ for the $3S_{1/2}$ state. It means that since $\ell=0$ there is only spin!
Anomalous Zeeman Effect

- In an external B field, each Dirac level splits into \((2j+1)\) sublevels ("magnetic substates")
- Each sublevel has a different value of \(m_j\)
- And the energy splitting is:

\[
E = E_{\text{Dirac}} + \Delta E
\]

\[
\Delta E = m_j q \mu_B B
\]
Anomalous Zeeman Effect

Let’s look at this effect for the $n=3$ energy levels in the H atom in an external B field:

\[
\begin{align*}
\text{Values of } m_j
\end{align*}
\]
Radiative transitions

- Let’s consider the \( n=3 \rightarrow n=2 \) transition.
- If \( B=0 \), then the energy of the radiated photon is the Bohr energy:
  \[
  E_\gamma = -\frac{13.6 \text{eV}}{(3)^2} - \left(-\frac{13.6 \text{eV}}{(2)^2}\right) = 1.9 \text{eV}
  \]
- The g factors are:
  \[
  g(2s_{\frac{1}{2}}) = 2 \quad ; \quad g(3p_{\frac{1}{2}}) = \frac{\sqrt{3}}{3} \quad ; \quad g(3p_{\frac{3}{2}}) = \frac{2\sqrt{3}}{3}
  \]
- And, if: \( B \neq 0 \), \( \Delta E = m_j g \mu_B B \)
- The selection rules are:
  \[
  \Delta \ell = \pm 1, \quad \Delta j = 0, \pm 1, \quad \Delta m_j = 0, \pm 1
  \]
So the difference in the photon energy spectral lines will be (the total energy will be $E_{\text{Dirac}} + \Delta E \approx E_{\text{Bohr}} + \Delta E$):

$$\Delta \bar{E}_g = \Delta \bar{E}_e - \Delta \bar{E}_f = [(m_j g)_i - (m_j g)_f] \mu e B$$

So the photon line splits into 4
So the photon line splits into six equally spaced lines.

Recall the normal Zeeman effect predicted 3 equally spaced lines.
Zeeman Effect in Sodium

- The sodium spectrum has a bright doublet at 588.9950 and 589.5924 nm.
- These lines are emitted in a transition from the 3p to the 3s levels.
- The sodium doublet is further split by the application of an external magnetic field
  - Zeeman Effect
Animation

- [link](https://web.phys.ksu.edu/vqm/software/online/vqm/html/zeemanspec.html)
Summary/Announcements

Next time: Pauli exclusion principle, multi-electron atoms

Note - *I’m covering more details in lecture on atomic structure than is in your book.* Now also refer to:

- *I have made this also available at the MSLC.*

Next homework due on Monday Nov 20.

Note: Wed. Nov. 22 → Friday classes!