Quantum Mechanics and Atomic Physics

Lecture 20:
Spin/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
  - **Today**: 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:
  \[ \Delta E = g \mu_B B \text{ with } g = 1: \text{ Normal Zeeman Effect} \]

- **Today**: we will see that in many atoms (including Hydrogen) splitting is not \( \Delta E = 1 \mu_B B \). In this case \( g \neq 1 \). **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!
Last time: Normal Zeeman Effect

- When \( B \neq 0 \), each Bohr model photon line should split into exactly 3 equally spaced lines.
- This is called the (normal) **Zeeman Effect**

![Diagram of energy levels and magnetic field effects]

**Selection rules:**
\[
\Delta l = \pm 1, \quad \Delta m_l = 0, \pm 1
\]

**Allowed transitions:**

- 3d transitions
- 2p transitions

![Additional diagrams showing allowed transitions]
Photon energies are:

\[ E_{\gamma} = E_i - E_f = (E_i^{Bohr} + \Delta E_i) - (E_f^{Bohr} + \Delta E_f) \]
\[ = (E_i^{Bohr} - E_f^{Bohr}) + (m_{\ell_i})g\mu_BB - (m_{\ell_f})g\mu_BB \]
\[ = E_{\gamma}^{Bohr} - (\Delta m_{\ell})g\mu_BB \]

\[ \Delta m_{\ell} = m_{\ell_f} - m_{\ell_i} \ ; \ \Delta m_{\ell} = 0, \pm 1 \ ; \ E_{\gamma}^{Bohr} = -13.6eV \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \]

\[ \Delta m_{\ell} = -1 \rightarrow E_{\gamma} = E_{\gamma}^{Bohr} + g\mu_BB \]
\[ \Delta m_{\ell} = 0 \rightarrow E_{\gamma} = E_{\gamma}^{Bohr} \]
\[ \Delta m_{\ell} = +1 \rightarrow E_{\gamma} = E_{\gamma}^{Bohr} - g\mu_BB \]
(Normal) Zeeman Effect

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

- Experimental results:
  - Zeeman effect does occur, and in some atoms it is “normal” (i.e. \( \Delta E = g \mu_B B \))
  - In many atoms (including Hydrogen) splitting is not \( \Delta E = 1 \mu_B B \). \( \Delta E \) had right order of magnitude but \( g \neq 1 \). Zeeman effect is “anomalous”. (more on this next time)
  - 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!
Electron Spin Angular Momentum

- Electron must have a spin (or intrinsic) angular momentum:

\[
S = \sqrt{s(s+1)} \hbar, \quad s = \frac{\gamma}{2}
\]

\[
\Rightarrow S' = \sqrt{(\frac{1}{2})(\frac{3}{2})} \hbar = \frac{\sqrt{3}}{2} \hbar
\]
Space quantization

\[ s_3 = m s \hbar, \quad m_s = -s, -s+1, \ldots, +s \]

\( (\text{your book: } s_3 = s \hbar = \pm \sqrt{2} \hbar) \)

\[ s_3 = \pm \frac{1}{2} \hbar \]

\[ \cos \theta = \frac{s_3}{s} = \frac{\pm \frac{1}{2} \hbar}{\sqrt{\frac{13}{2} \hbar}} = \pm \frac{1}{\sqrt{3}} \]

\( \Rightarrow \theta = 55^\circ \text{ or } 125^\circ \)
If \( m_s = +1/2 \) we say electron is “spin up”

If \( m_s = -1/2 \) we say electron is “spin down”

\( m_s \) is called the magnetic spin quantum number

\( s \) is called the spin quantum number
Consequences of electron spin

- Electron spin creates a spin magnetic moment.
- Electron’s orbital motion creates an internal magnetic field in an atom.
- The two interact to cause a splitting of energy levels even if $B_{\text{external}} = 0$.

\[ \hat{\mu}_L = -g \frac{e}{2mL} \hat{L}, \quad g = 1 \]
\[ \hat{\mu}_S = -g \frac{e}{2mS} \hat{S}, \quad g = \frac{2}{3} \, \text{predicted by} \]
\[ \text{relativistic QM, (Dirac equation)} \]
Four quantum numbers

To understand the H atom we need these four quantum numbers:

1. \( n \): expresses quantization of energy
2. \( l \): quantizes magnitude of \( \mathbf{L} \)
3. \( m_l \): quantizes direction of \( \mathbf{L} \)
4. \( m_s \): quantizes direction of \( \mathbf{S} \)

\( s \) is left out because it has the single value of \( s=1/2 \).

It quantizes the magnitude of \( \mathbf{S} \).
Stern-Gerlach Experiment (1922)

- Showed the quantization of electron spin into two orientations

- *Electron spin was unknown at the time!*
  - They wanted to demonstrate the space quantization associated with electrons in atoms

- Used a beam of silver atoms from a hot oven directed into a region of non-uniform magnetic field

- The silver atoms allowed Stern and Gerlach to study the magnetic properties of a single electron
  - a single outer electron: 47 protons of the nucleus shielded by the 46 inner electrons
  - Expected $2\ell + 1$ splittings from space quantization of orbital moments (classically it would be a continuous distribution)
  - Also note: this electron (ground state) has zero orbital angular momentum
    - Therefore, expect there to be no interaction with an external magnetic field.
Schematic of experiment

Photographic plate

Beam of silver atoms

Magnet pole

Inhomogeneous magnetic field

Field on

Zero field pattern

Classical expectation

Experimental result

Spin can take only two orientations

$\frac{1}{2} \hbar$

$\frac{\sqrt{3}}{2} \hbar$

Oven
What they expected/saw

- Expected $2\ell + 1$ splittings from space quantization of orbital moments.
- Classically one would expect all possible orientations of the dipoles so that a continuous smear would be produced on the photographic plate.
- They found that the field separated the beam into two distinct parts, indicating just two possible orientations of the magnetic moment of the electron!
In external B-field ...

\[ \vec{\mu}_S = -g \frac{e}{2m} \hat{S} \]
\[ \Delta E_S = -\vec{\mu}_S \cdot \vec{B} = +g \frac{e}{2m} B \cdot \hat{S}_z = \frac{e}{2m} B \]
\[ \Rightarrow \Delta E_S = (\pm \frac{1}{2}) (2) \mu_B B = \pm \mu_B B \]

- A magnetic dipole moment will experience a force proportional to the field gradient since the two "poles" will be subject to different fields.
In inhomogeneous B field, 

\( m_s = +1/2 \) is deflected up and 

\( m_s = -1/2 \) is deflected down.
Interactive simulation

http://phet.colorado.edu/simulations/sims.php?sim=SternGerlach_Experiment
How does the electron obtain a magnetic moment if it has zero angular momentum and therefore produces no "current loop" to produce a magnetic moment?

In 1925, Goudsmit and Uhlenbeck postulated that the electron had an intrinsic angular momentum, independent of its orbital characteristics.

Led to the use of "electron spin" to describe the intrinsic angular momentum.
Summary of electron states

Reed: chapter 8

Table 8.1 Electron States.

<table>
<thead>
<tr>
<th>n</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>l</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>m</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>s</td>
<td>±1/2</td>
<td>±1/2</td>
<td>±1/2</td>
</tr>
<tr>
<td>States</td>
<td>2</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Subshell</td>
<td>1s</td>
<td>2s</td>
<td>2p</td>
</tr>
<tr>
<td>Shell</td>
<td>K</td>
<td>L</td>
<td>M</td>
</tr>
<tr>
<td>Total states</td>
<td>2</td>
<td>8</td>
<td>18</td>
</tr>
</tbody>
</table>

\[
B \neq 0
\]
Energy Level Diagrams

B=0

\[
\begin{array}{cccccc}
   l = 0 & 1 & 2 & 3 & 4 & 5 \\
   \text{BOHR THEORY} & \text{SCHRODINGER THEORY} \\
   2s(2s) & l=0 & l=1 & l=2 & l=3 \\
   -\frac{13.6}{16} & 4s & 4p & 4d & 4f \\
   -\frac{13.6}{9} & 3s & 3p & 3d \\
   -\frac{13.6}{4} & 2s & 2p \\
   -13.6 & 1s \\
\end{array}
\]

B\neq 0

\[
\begin{array}{cccccc}
   l = 0 & l = 1 & l = 2 \\
   \text{ENERGY (eV)} \\
   -\frac{13.6}{(3)^2} & 3s & 3p & 3d \\
   -\frac{13.6}{(2)^2} & 2s & 2p \\
   -13.6 & 1s \\
\end{array}
\]

\text{VALUES OF } m_l
Spin-Orbit Coupling

- **The magnetic moments are:**

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

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

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

“Vector model” of angular momentum:

- **Total** angular momentum is:

\[ \mathbf{J} = \mathbf{L} + \mathbf{S} \]

- \( J = |\mathbf{J}| = \sqrt{j(j+1)} \hbar \)

- \( J_z = m_j \hbar \)

- J precesses about the z-axis

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 $s=1/2$

- 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:
  \[ E_{\text{Bohr}} = -13.6 \text{eV} \cdot \frac{1}{n^2} \]
  \[ E_{\text{Bohr}} = -\frac{1}{2} m c^2 \frac{a^2}{n^2} \]

- 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:

- Since $s=1/2$ in Hydrogen, $2s+1=2$ always.

- Example:
  - $n=4$, $\ell=1$, $j=3/2$
  - 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/Shroedinger theory

$B_{\text{external}} = 0$
Summary/Announcements

- Next time: Finish Zeeman Effect, 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 18.
- Note: Wed. Nov. 27 → Friday classes!
- Final exam: Dec. 18, 8-11am, SEC 210 (note room!)