Quantum Mechanics and Atomic Physics

Lecture 20:
Real Hydrogen Atom /Identical particles
http://www.physics.rutgers.edu/ugrad/361
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Last time

- Hydrogen atom: electron in circular orbit
  - creates an orbital magnetic 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:
  \[ \Delta E = g \mu_B B \]  with \( g = 1 \): **Normal Zeeman Effect**:
  In reality, many more lines exist, and was called Anomalous Zeeman Effect; will not be covered in this course.

- Radiative Transitions (Photon emission or absorption) occur only between
  \[ \Delta l = \pm 1 \text{ and } \Delta m_l = 0, \pm 1 \]

  This is called Selection Rules.
Energy Level Diagrams for Simple Hydrogen Model

$B=0$

$B \neq 0$
Real Hydrogen Atom

- Energy levels split even in the absence of B field due to
  1. Spin-orbit coupling (fine structure):
     - Relativistic effect (Dirac theory), \( \sim 10^{-4} \text{ eV} \)
  2. Electron-nucleon spin interaction (hyperfine structure): \( \sim 10^{-6} \text{ eV} \)
  3. Quantum electrodynamics effect (Lamb shift):
     - \( \sim 10^{-6} \text{ eV} \)

We will cover each of these briefly today.
Energy scales of each effect

\[ \alpha = \frac{e^2}{4\pi \hbar c} \approx \frac{1}{137} \quad : \text{Fine structure constant} \]

- Electron mass: \( mc^2 : \sim 0.5 \text{ MeV} \)
- Bohr energies: of order \( \alpha^2 mc^2 : \sim 10 \text{ eV} \)
- Fine structure: of order \( \alpha^4 mc^2 : \sim 10^{-4} \text{ eV} \)
- Lamb shift: of order \( \alpha^5 mc^2 : \sim 10^{-6} \text{ eV} \)
- Hyperfine splitting: of order \( (m/m_p) \alpha^4 mc^2 : \sim 10^{-6} \text{ eV} \)
Spin-Orbit Coupling

- The magnetic moments are:

\[
\begin{align*}
\vec{\mu}_l &= -g \frac{e}{2m} \vec{l} \\
\vec{\mu}_s &= -g \frac{e}{2m} \vec{s}
\end{align*}
\]

- Interaction of \( \mu_L \) and \( \mu_S \) causes a **fine-structure splitting** of energy levels, even if \( B_{\text{external}} = 0 \)!
Origin of Spin-Orbit Coupling

- In electron's reference frame (neglect that it is not inertial), special relativity says that

\[
\vec{B} = -\frac{\vec{v} \times \vec{E}}{c^2}, \quad \vec{E} = \frac{e \vec{r}}{4\pi \epsilon_0 r^3}, \quad \vec{v} = \frac{\vec{p}}{m_e}
\]

\[
\Rightarrow \vec{B} = -\frac{\vec{p} \times \vec{r}^3}{2m_e c^2} \left( \frac{e}{4\pi \epsilon_0 r^3} \right) = \vec{r} \times \vec{p} \left( \frac{e}{4\pi \epsilon_0 m_e c^2 r^3} \right)
\]

\[
= \vec{r} \cdot \left( \frac{e}{4\pi \epsilon_0 m_e c^2 r^3} \right)
\]

Thus

\[
\Delta H = -\vec{m}_e \cdot \vec{B} = -\frac{e}{2m} \frac{\text{const}}{r^3} = \frac{\text{const}}{r^3} \Rightarrow S \cdot \vec{L}
\]
Spin-Orbit effect, con’t

It turns out that the spin-orbit effect plus relativistic correction \( KE = \sqrt{p^2 c^2 + m^2 c^4} - mc^2 \) provides

\[
E_{\text{Dirac}} = E_{\text{Born}} \left[ 1 + \frac{\alpha^2}{n} \left( \frac{1}{j+y} - \frac{3}{4n} \right) \right]
\]

This result is obtained by Dirac.

Here, \( j \) is the total angular momentum quantum number corresponding to \( \vec{J} = \vec{L} + \vec{S} \)
Spin-Orbit Coupling, con’t

- “Vector model” of angular momentum:
  - Total angular momentum is:
    \[ J = L + S \]
    \[ J = |J| = \sqrt{J(J+1)} \hbar \]
    \[ J_z = m_j \hbar \]

- 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: \( n, \ell, m_\ell, m_s \)
Angular momentum Addition

Angular momentum addition is itself a whole new non-trivial subject, and here I just list the final results:

\[ \mathbf{J} = \mathbf{L}_1 + \mathbf{L}_2 \quad \text{with} \quad \mathbf{L}_i \leftrightarrow l_i, m_{e_i} \]

\[ \mathbf{J} \leftrightarrow \mathbf{j}, m_j \]

\[ j = l_1 - l_2, |l_1 - l_2| + 1, \ldots, l_1 + l_2 \]

\[ m_j = m_{e_1} + m_{e_2} \]
Hydrogen Fine-Structure

- Only one electron in Hydrogen so \( s = 1/2 \)

- Most of the Schrödinger 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

- The Bohr energy levels are:
  \[ E_{\text{Bohr}} = -13.6 \text{ eV} = -\left(\frac{1}{2} \alpha^2 m c^2\right) \frac{1}{n^2} \]
  \( \text{order} \ \alpha^2 m c^2 \)

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

- Now, in the Dirac theory:
  \[ E_{\text{Dirac}} = E_{\text{Bohr}} \left[ 1 + \frac{\alpha^2}{n} \left( \frac{1}{j + \frac{3}{2}} - \frac{3}{4n} \right) \right] \]
  \[ \Rightarrow \Delta H \approx -\alpha^2 E_{\text{Bohr}} \text{; order} \ \alpha^4 m c^2 \]

- 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

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

\[
\Delta E_{F5} = E_{Bohr} \left[ \frac{\alpha^2}{n} \left( \frac{1}{j+y_2} - \frac{3}{4n} \right) \right] \\
= -13.6 \text{eV} \left[ \frac{1}{15^2} \left( \frac{1}{1} \right) \left( \frac{1}{y_2+y_2} - \frac{3}{4(1)} \right) \right] \\
= -13.6 \text{eV} \left[ \frac{1}{15^2} \left( \frac{1}{4} \right) \right] \\
= -13.6 \text{eV} \left( 1.33 \times 10^{-5} \right) \\
= -1.81 \times 10^{-4} \text{eV}
\]

- A little below the Bohr value
Example

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

\[ E_{n=2} : \quad E_{\text{Bohr}} = -\frac{13.6\text{eV}}{2^2} = -3.4\text{eV} \]

\[ \Delta E_{F_5}(j=\frac{1}{2}) = -(3.4\text{eV}) \left( \frac{1}{i37} \right)^2 \left( \frac{1}{2} \right) \left( \frac{1}{y_2 y_2} - \frac{3}{4.2} \right) \]

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

\[ \Delta E_{F_5}(j=\frac{3}{2}) = -(3.4\text{eV}) \left( \frac{1}{i37} \right)^2 \left( \frac{1}{2} \right) \left( \frac{1}{\gamma_2 y_2} - \frac{3}{4.2} \right) \]

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

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

- This is why it’s called “fine” structure!
Hyperfine Structure

- Proton and neutrons are also spin 1/2 particles
- So nuclear spin angular momentum can interact with the electron’s $\mu_j$ to split each Dirac energy level into two!
- But … it’s a very tiny effect
  - Because $m_{\text{proton}} \gg m_{\text{electron}}$
  - $\vec{\mathbf{M}} = g \frac{e}{2m} \vec{S}$
  - $\Delta H \approx (\frac{m}{m_p}) \alpha^4 \frac{m c^2}{E}$
- Hyperfine splitting is $\sim 10^{-6}$ eV
There’s even more to the story

- In 1947, Willis Lamb discovered that the $2P_{1/2}$ state is slightly lower than the $2S_{1/2}$ state resulting in a slight shift of the corresponding spectral line.
  - This is called the Lamb shift.

![Lamb Shift Diagram]

- One would think that such a tiny effect would be considered insignificant.
- But later Hans Bethe was the first to explain the Lamb shift in the hydrogen spectrum.
  - Beginning of the modern development of quantum electrodynamics!
Energy Level diagram revisited

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

- Without Lamb shift they should be equal.
Quantum Electrodynamics (QED)

- Developed by Feynman, Schwinger, and Tomonaga in the 1940’s
- The electromagnetic force is transmitted via the exchange of virtual photons
- Example: Scattering of one electron off another

This is called a Feynman Diagram
Higher-order effects in QED

Interactions with the “vacuum”

<table>
<thead>
<tr>
<th></th>
<th>QED Theory</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron’s g factor</td>
<td>2.002319282 ± 0.000000006</td>
<td>2.002319288 ± 0.000000014</td>
</tr>
<tr>
<td>Fine-Structure</td>
<td>1.096903x10^{10}\text{Hz} ± 0.000004</td>
<td>1.096913x10^{10}\text{Hz} ± 0.000010</td>
</tr>
<tr>
<td>(2P_{3/2} - 2P_{1/2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lamb Shift</td>
<td>1.05791x10^{9}\text{Hz} ± 0.00016</td>
<td>1.05790x10^{9}\text{Hz} ± 0.00006</td>
</tr>
<tr>
<td>(2P_{1/2} - 2S_{1/2})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hyperfine</td>
<td>1.4204057x10^{9}\text{Hz} ± 0.0000001</td>
<td>1.4204057517864x10^{9}\text{Hz} ± 0.0000000001</td>
</tr>
<tr>
<td>21cm line</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Electron emits and reabsorbs a virtual photon

Photon's g factor: 2.002319282 ± 0.000000006

Fine-Structure: 1.096903x10^{10}\text{Hz} ± 0.000004

Lamb Shift: 1.05791x10^{9}\text{Hz} ± 0.00016

Hyperfine: 1.4204057x10^{9}\text{Hz} ± 0.0000001

Photons are continuously turning into e^+e^- pairs and then annihilating them back into photons

Amazing agreement!
The true energy levels of Hydrogen

For B=0
Energy scales of each effect

\[ \alpha = \frac{e^2}{4\pi\hbar c} \approx \frac{1}{137} \] : Fine structure constant

- Electron mass : \( mc^2 \): \( \sim 0.5 \text{ MeV} \)
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- Lamb shift: of order \( \alpha^5 mc^2 \): \( \sim 10^{-6} \text{ eV} \)
- Hyperfine splitting: of order \( \alpha^4 mc^2 \): \( \sim 10^{-6} \text{ eV} \)
Multi-Electron Atoms

- Atoms with 2 or more electrons have a new feature:
  - Electrons are indistinguishable!
  - There is no way to tell them apart!
- Any measurable quantity (probability, expectation value, etc.) must not depend on which electron is labeled 1, 2, etc.
S.E. for Multi-electron atoms

- Let’s consider two electrons in Helium with coordinates:

\[ (x_1, y_1, z_1) \quad (x_2, y_2, z_2) \]

or

\[ (\vec{r}_1) \quad (\vec{r}_2) \]

- The total Hamiltonian operator for this system is

\[ H_{2e} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V_{\text{tot}} \]

- So the Schrodinger equation is:

\[ -\frac{\hbar^2}{2m_1} \nabla_1^2 \psi_{\text{tot}} - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi_{\text{tot}} + V_{\text{tot}} \psi_{\text{tot}} = E_{\text{tot}} \psi_{\text{tot}} \]
S.E. for Multi-electron atoms

- The total potential $V_{\text{tot}}$ has 3 contributions:
  1. $V$ between electron 1 and the nucleus
  2. $V$ between electron 2 and the nucleus
  3. $V$ between electron 1 and electron 2

- For now, let’s consider only #1 and #2

- So,
  
  $$ V_{\text{Tot}} = V_1 (x_1, y_1, z_1) + V_2 (x_2, y_2, z_2) $$

  or

  $$ V_{\text{Tot}} = V_1 (\vec{r}_1) + V_2 (\vec{r}_2) $$

- Note that the potential function is the same for both electrons
S.E. for Multi-electron atoms

\[-\frac{\hbar^2}{2m_1} \nabla^2 \Psi_{\text{tot}} - \frac{\hbar^2}{2m_2} \nabla^2 \Psi_{\text{tot}} + V_1 \Psi_{\text{tot}} + V_2 \Psi_{\text{tot}} = \varepsilon_{\text{tot}} \Psi_{\text{tot}}\]

- We get the usual separation of variables
  \[\Psi_{\text{tot}} = \Psi_A (x_1, y_1, z_1) \Psi_B (x_2, y_2, z_2)\]

- Each \(\Psi\) will depend on quantum numbers \(n, \ell, m_\ell, m_s\)

- So, \(A\) and \(B\) stand for the particular sets of quantum numbers

- So, let’s call \(\Psi_A(1)\) eigenfunction for electron #1 and has the quantum numbers symbolized by \(A\).
S.E. for Multi-electron atoms

- So, total eigenfunction solution is:

\[ \psi_{\text{Tot}} = \psi_A (i) \psi_B (z) \]

- And with this separability assumption, the S.E. becomes:

\[
- \frac{\hbar^2}{2m_1} \nabla_1^2 \psi_A \psi_B - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi_A \psi_B + V_1 \psi_A \psi_B + V_2 \psi_A \psi_B = E_{\text{Tot}} \psi_A \psi_B
\]

\[
\left\{ - \frac{\hbar^2}{2m_1} \nabla_1^2 \psi_A + V_1 \psi_A \right\} \psi_3 + \left\{ - \frac{\hbar^2}{2m_2} \nabla_2^2 \psi_B + V_2 \psi_B \right\} \psi_4 = E \psi_3 \psi_4
\]

- This equation suggests that we write the total energy \( E \) as:

\[ E = E_A + E_B \]
S.E. for Multi-electron atoms

- So, we can separate this neatly into two independent expressions:

\[-\frac{\hbar^2}{2m_i} \nabla_i^2 \Psi_A + V_i \Psi_A = E_A \Psi_A\]

\[-\frac{\hbar^2}{2m_j} \nabla_j^2 \Psi_B + V_j \Psi_B = E_B \Psi_B\]

- (This can be extended to any number of non-interacting particles!)
Exchange electrons

- So, we said that the total eigenfunction is:
  \[ \Psi_{\text{tot}} = \Psi_A(1) \Psi_B(2) \]

- If we exchange electrons 1 and 2 we get:
  \[ \Psi_{\text{tot}} = \Psi_B(1) \Psi_A(2) \]

- But the first equation gives:
  \[ \Psi_A^* \Psi = \Psi_A^*(1) \Psi_B^*(2) \Psi_A(1) \Psi_B(2) \]

- And the second (exchanged) equation gives:
  \[ \Psi_B^* \Psi_{\text{tot}} = \Psi_A^*(2) \Psi_B^*(1) \Psi_A(2) \Psi_B(1) \]

- But these two probabilities are different!
  - This is not acceptable!
  - This means that the expressions for \( \Psi_{\text{tot}} \) above are not valid solutions!
Exchange electrons

- Since:
  \[ \psi \ast \psi = |\psi|^2 \]

- We need this to be satisfied:
  \[ |\Psi_{\text{after exchange}}|^2 = |\Psi_{\text{before exchange}}|^2 \]

- So the total eigenfunction:
  \[ \Psi_{\text{after exchange}} = \pm \Psi_{\text{before exchange}} \]

- + sign: Symmetric eigenfunction \( \Psi_{\text{Symm}} \)
- - sign: Antisymmetric eigenfunction \( \Psi_{\text{Anti}} \)
Symmetric and Antisymmetric

\[
\Psi_{\text{Symm}} = \frac{1}{\sqrt{2}} \left[ \psi_A(1) \psi_B(2) + \psi_B(1) \psi_A(2) \right]
\]

\[
\Psi_{\text{Anti}} = \frac{1}{\sqrt{2}} \left[ \psi_A(1) \psi_B(2) - \psi_B(1) \psi_A(2) \right]
\]

- \(\Psi_{\text{Symm}}\) and \(\Psi_{\text{Anti}}\) are degenerate!
  - Same energy
  - They exhibit “exchange degeneracy”
- They have the right properties:
  \[
  \Psi_{\text{Symm}} \text{ (after exchange)} = \Psi_{\text{Symm}} \text{ (before exchange)}
  \]
  \[
  \Psi_{\text{Anti}} \text{ (after exchange)} = -\Psi_{\text{Anti}} \text{ (before exchange)}
  \]
- Note \(1/\sqrt{2}\) is for normalization, assuming that \(\Psi_{\text{tot}}\) is normalized:

\[
\int \psi_{\text{Symm}}^* \psi_{\text{Symm}} \, d\chi = \frac{1}{2} \left[ \int \psi_{\text{tot}}^* \psi_{\text{tot}} + \int \psi_{\text{tot}}^* \psi_{\text{tot}} \right] = 1
\]
Pauli Exclusion Principle

- Principle was formulated by Wolfgang Pauli in 1925.
- “Weak form”:
  - In an atom, no two electrons can be in the same quantum state, i.e. the same set of quantum numbers: $n, \ell, m_\ell, m_s$
Pauli Exclusion Principle

- Suppose electrons 1 and 2 are in the same quantum state A. Then:

\[ \Psi_{\text{symm}} = \frac{1}{\sqrt{2}} \left[ \psi_1(1) \psi_2(2) + \psi_1(1) \psi_2(2) \right] \]

\[ = \sqrt{2} \psi_1(1) \psi_2(2) \neq 0 \]

- So, \( \Psi_{\text{symm}} \) permits 2 electrons in the same state.
- So, \( \Psi_{\text{symm}} \) violates the Pauli exclusion principle

\[ \Psi_{\text{anti}} = \frac{1}{\sqrt{2}} \left[ \psi_1(1) \psi_2(2) - \psi_1(1) \psi_2(2) \right] = 0 \]

- \( \Psi_{\text{anti}} \) obeys the Pauli exclusion principle.
Pauli Exclusion Principle

“Strong” form of Pauli Exclusion Principle:

- A multi-electron system must have an antisymmetric total eigenfunction.
- “Strong” because it also incorporates indistinguishability.
- All particles of half-integer spin (1/2, 3/2, …) have antisymmetric total eigenfunctions and are called “Fermions”, obeying Fermi-Dirac statistics
  - Electrons, protons, neutrons
- All particles of integer spin (0, 1, 2, …) have symmetric total eigenfunctions, and are called “Bosons”, obeying Bose-Einstein statistics.
  - Photons, alpha, W and Z particles

\[
\Psi_{tot} \propto \Psi_A(1)\Psi_B(2) \pm \Psi_A(2)\Psi_B(1)
\]

Required for Bosons

Required for Fermions
Summary/Announcements

- Next time: More on Pauli exclusion and multi-electron atoms

- Next homework due on Monday Nov 28.

- No class coming Wednesday, November 23 – Thanksgiving recess