Quantum Mechanics and Atomic Physics

Lecture 22: Multi-electron Atoms

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

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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></td>
<td></td>
</tr>
<tr>
<td>2P_{3/2} - 2P_{1/2}</td>
<td>1.096903\times10^{10}Hz ± 0.000004</td>
<td>1.096913\times10^{10}Hz ± 0.000010</td>
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<tr>
<td>Lamb Shift</td>
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<td></td>
</tr>
<tr>
<td>2P_{1/2} - 2S_{1/2}</td>
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<td>1.05790\times10^{9}Hz ± 0.00006</td>
</tr>
<tr>
<td>Hyperfine</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21cm line</td>
<td>1.4204057\times10^{9}Hz ± 0.0000001</td>
<td>1.4204057517864\times10^{9}Hz ± 0.0000000001</td>
</tr>
</tbody>
</table>

Electron emits and reabsorbs a virtual photon

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

Amazing agreement!
The true energy levels of Hydrogen

For $B=0$

Fine Structure splitting, Lamb shift and Zeeman effect

Fine structure

The Lamb shift is about one tenth as large as the fine structure splitting
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:

\[
\begin{align*}
\left( x_1, y_1, z_1 \right) & \quad \left( x_2, y_2, z_2 \right) \\
\left( \hat{r}_1 \right) & \quad \left( \hat{r}_2 \right)
\end{align*}
\]

- The total Hamiltonian operator for this system is

\[
H_{op} = -\frac{\hbar^2}{2m_1} \nabla_1^2 - \frac{\hbar^2}{2m_2} \nabla_2^2 + V_{tot} \quad \text{(of course, in this case } m_1 = m_2)\]

- So the Schrödinger equation is:

\[
-\frac{\hbar^2}{2m_1} \nabla_1^2 \Psi_{tot} - \frac{\hbar^2}{2m_2} \nabla_2^2 \Psi_{tot} + V_{tot} \Psi_{tot} = E_{tot} \Psi_{tot}
\]
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

$$V_{\text{Tot}} = V_1(r_1) + V_2(r_2)$$

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

\[-\frac{\hbar^2}{2m_1} \nabla^2_1 \Psi_{tot} - \frac{\hbar^2}{2m_2} \nabla^2_2 \Psi_{tot} + V_{tot} \Psi_{tot} = E_{tot} \Psi_{tot}\]

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

- 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:

\[ \psi_{\text{Tot}} = \psi_A(1) \psi_B(2) \]

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

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

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

- 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:

\[
- \frac{\hbar^2}{2m_1} \nabla_i^2 \psi_A + V_1 \psi_A = \varepsilon_A \psi_A
\]

\[
- \frac{\hbar^2}{2m_2} \nabla_2^2 \psi_B + V_2 \psi_B = \varepsilon_B \psi_B
\]

- (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:
  \[ \Psi^\times \Psi_{\text{Tot}} = \Psi_A^\times(1) \Psi_B^\times(2) \Psi_A(1) \Psi_B(2) \]

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

- 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:

\[ \psi \times \psi = |\psi|^2 \]

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 $\Psi$

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

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

- $\Psi_{\text{Symm}}$ 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
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:

\[ \psi_{\text{symm}} = \frac{1}{\sqrt{2}} [\psi_A(1) \psi_A(2) + \psi_A(1) \psi_A(2)] \]

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

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

\[ \psi_{\text{anti}} = \frac{1}{\sqrt{2}} \left( \psi_A(1) \psi_A(2) - \psi_A(1) \psi_A(2) \right) = 0 \]

- So \( \psi_{\text{anti}} \) 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

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

- Normal Helium ($^4_2$ He)
  - 2 protons, 2 neutrons and 2 electrons
  - Even number of spin $\frac{1}{2}$ constituents
  - Is a Boson

- Helium-3 ($^3_2$ He)
  - 2 protons, 1 neutrons, 2 electrons
  - Odd number of spin $\frac{1}{2}$ constituents
  - Is a Fermion
Total Fermion Eigenfunction

- So, for Fermion, total eigenfunction must be antisymmetric

- Can write:

\[ \Psi_{\text{Anti}} = \Psi_{\text{space}} \Psi_{\text{spin}} \]

- So, \( \Psi_{\text{space}} \) and \( \Psi_{\text{spin}} \) must have opposite symmetry in order for \( \Psi_{\text{Anti}} \) to be antisymmetric

- We had used A and B as abbreviations for particular sets of \( n, \ell, m_\ell, m_s \)

- Now let’s use a and b as abbreviations for particular sets of \( n, \ell, m_\ell \)
  - i.e. just the space part
Space and Spin Eigenfunctions

\[ \Psi_{\text{symm}}(\text{space}) = \frac{1}{\sqrt{2}} \left[ \Psi_a(1) \Psi_b(2) + \Psi_b(1) \Psi_a(2) \right] \]

\[ \Psi_{\text{anti}}(\text{space}) = \frac{1}{\sqrt{2}} \left[ \Psi_a(1) \Psi_b(2) - \Psi_b(1) \Psi_a(2) \right] \]

- The space wavefunctions are analogous to \( R\Theta\Phi \) for Hydrogen

- Spin wavefunctions are matrices
  - Symbolically,
Spin Eigenfunctions

- Let’s write this such that $\chi$ has a definite symmetry

- So, the antisymmetric $\chi$, corresponding to $\Psi_{\text{Symm}}(\text{space})$ (singlet state):
  \[
  \chi_{\text{Anti}} = \frac{1}{\sqrt{2}} \left[ \chi(\frac{1}{2}, -\frac{1}{2}) - \chi(-\frac{1}{2}, \frac{1}{2}) \right]
  \]

- The symmetric $\chi$, corresponding to $\Psi_{\text{Anti}}(\text{space})$; there are three ways to do it (triplet state):
  \[
  \chi_{\text{Symm}} = \begin{cases} 
  \chi \quad (+1/2,+1/2) \\
  \frac{1}{\sqrt{2}} \left[ \chi(\frac{1}{2}, -\frac{1}{2}) + \chi(-\frac{1}{2}, \frac{1}{2}) \right] \\
  \chi \quad (-1/2,-1/2)
  \end{cases}
  \]
Spin Angular Momentum

In a two electron atom (Helium) the spin angular momentum of the two electrons couple to give the total spin:

\[ \vec{S'} = \vec{S}_1 + \vec{S}_2 \]

\[ S' = |\vec{S'}| = \sqrt{S'(S'+1)} \hbar \]

\[ S'_z = m_s \hbar \]

\[ m_s' = -S', -S'+1, \ldots, +S' \]

But what is s’?

\[ S_1 = S_2 = \frac{1}{2} \]

\[ S' = |S_1 - S_2|, |S_1 - S_2| + 1, \ldots, (S_1 + S_2) \]

= 0 or 1
Spin Angular Momentum

- If \( s' = 0 \), \( m_{s'} = 0 \) only, and this is the singlet state, which is antisymmetric.
  - We have opposite spins, and \( S' = 0 \)

- If \( s' = 1 \), \( m_{s'} = -1, 0, +1 \), and this is why we get the triplet state which is symmetric.
  - We have “parallel” spins
Parallel Spins

- For “parallel” spins:
  - \( s' = 1 \)
  - triplet state in Helium
  - \( \chi \) symmetric
  - \( \Psi(\text{space}) \) antisymmetric.

- Suppose electrons get close, so \( a = b \) (same spacial quantum numbers):

\[
\Psi_{\text{Anti (space)}} = \frac{1}{\sqrt{a}} \left[ \Psi_a(1) \Psi_a(2) - \Psi_a(1) \Psi_a(2) \right] = 0
\]

- Low probability for electrons to have similar coordinates
- Parallel-spin electron repel each other, over and above the Coulomb repulsion.
- This “exchange” force mainly reflects the exclusion principle
Antiparallel Spins

- For antiparallel spins:
  - $s'=0$
  - Singlet state in Helium
  - $\chi$ antisymmetric
  - $\Psi$(space) symmetric

- Suppose electrons get close, so $a=b$ (same spacial quantum numbers):

$$\Psi_{\text{Symm (space)}} = \frac{1}{\sqrt{2}} [\Psi_a(1)\Psi_a(2) + \Psi_a(1)\Psi_a(2)] = \sqrt{2} \Psi_a(1)\Psi_a(2)$$

- This is large, so antiparallel-spin electrons attract each other via the “exchange” force.
Summary:

- **Multi-electron atoms and Pauli’s exclusion principle**
- Electrons are Fermions (spin 1/2), are indistinguishable and have an antisymmetric total eigenfunction

\[ \Psi_{\text{anti}} = \Psi(\text{space}) \Psi(\text{spin}) \]

- **Helium:**
  - For antiparallel spins:
    - \( s' = 0 \)
    - Singlet state in Helium
    - \( \chi \) antisymmetric
    - \( \Psi(\text{space}) \) symmetric
  - For parallel spins:
    - \( s' = 1 \)
    - triplet state in Helium
    - \( \chi \) symmetric
    - \( \Psi(\text{space}) \) antisymmetric.
Example

If we put 5 electrons (fermions!) in an infinite square well, what is the ground state energy?

Recall the energies for an infinite square well are:

$$E_n = \frac{n^2 \pi^2 \hbar^2}{2mL^2} = n^2 E_1,$$
where

$$E_1 = \frac{\pi^2 \hbar^2}{2mL^2}.$$

Since electrons are fermions, 2 electrons will populate n=1, 2 in n=2, and 1 in n=3.

So, the ground state energy of this system is:

$$E = 2 \cdot (E_1) + 2 \cdot (4E_1) + 1 \cdot (9E_1) = 19E_1.$$

What if we put 5 bosons in the well?

All 5 bosons can go into n=1!

So ground state energy is E=5E_1
Complex Atoms

- For complex atoms, S.E. is solved numerically (we’ll see this in Reed Chapter 10) using:
  - the potential between each electron and the nucleus,
  - and the potential between each electron and all the others.
- Atomic energy levels and chemical properties are then obtained!

Each value of \( n \) corresponds to a shell:
\[
\begin{align*}
n: & \quad 1 \quad 2 \quad 3 \quad 4 \quad \ldots \\
\text{Shell:} & \quad \text{K} \quad \text{L} \quad \text{M} \quad \text{N} \quad \ldots
\end{align*}
\]

Each \( n \) and \( \ell \) constitute a subshell:
\[
\begin{align*}
\ell: & \quad 0 \quad 1 \quad 2 \quad 3 \quad 4 \quad \ldots \\
& \quad \text{s} \quad \text{p} \quad \text{d} \quad \text{f} \quad \text{g} \quad \ldots
\end{align*}
\]
## Population of Shells

<table>
<thead>
<tr>
<th>Shell</th>
<th>n</th>
<th>( \ell )</th>
<th>( m_\ell )</th>
<th>( m_s )</th>
<th>Sub-shell</th>
<th>Max. Sub-shell population</th>
<th>Max. Shell population</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>±1/2</td>
<td>1s</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>L</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>±1/2</td>
<td>2s</td>
<td>2</td>
<td>8</td>
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<tr>
<td></td>
<td></td>
<td>1</td>
<td>0, ±1</td>
<td>±1/2</td>
<td>2p</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>±1/2</td>
<td>3s</td>
<td>2</td>
<td>18</td>
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<td></td>
<td>1</td>
<td>0, ±1</td>
<td>±1/2</td>
<td>3p</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>0, ±1, ±2</td>
<td>±1/2</td>
<td>3d</td>
<td>10</td>
<td></td>
</tr>
</tbody>
</table>

For each \( \ell \), there are \((2\ell+1)\) values of \( m_\ell \) and 2 values of \( m_s \), so the maximum subshell population is \(2(2\ell+1)\)
Summary/Announcements

- **Next time:**
  - Multi-electrons continued, and in a B field
  - Approximation Methods (I)

- **Next HW due Monday Nov. 25**

- **Quiz next Monday, Nov. 25 on Chapter 7.**

- **Next Wednesday, November 27 we have no class**
  - Wednesday ➔ Friday classes

- **Final exam: Wed. Dec 18th 8-11am room SEC 10**
  - More details to come soon