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:

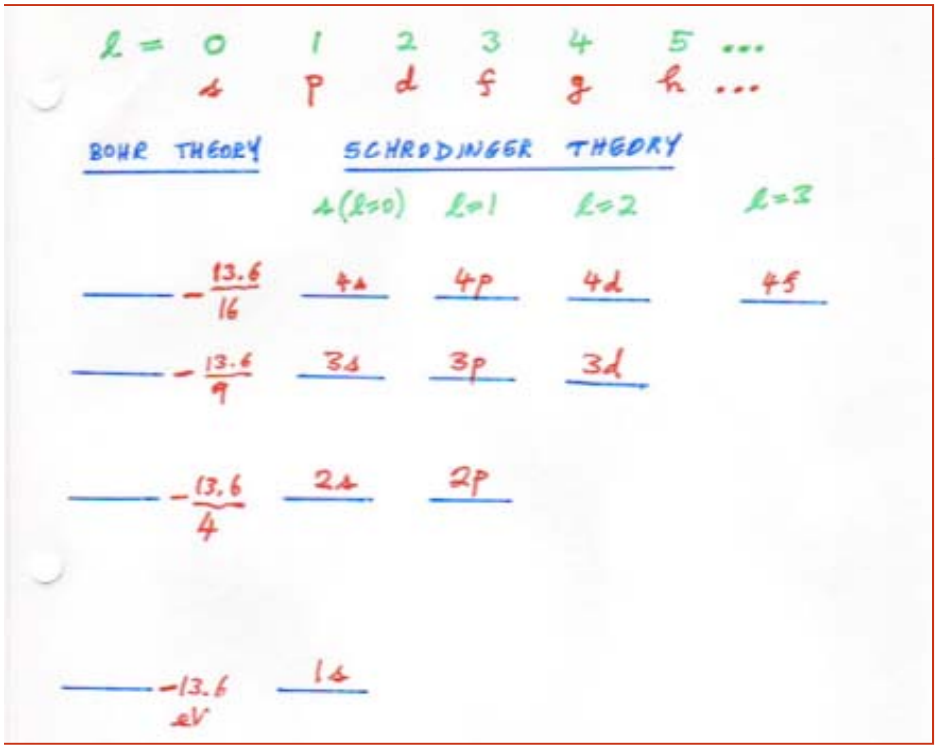
  $\Delta E = g\mu_B B$ with $g=1$: Normal Zeeman Effect:

  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 $\Delta \ell = \pm 1$ and $\Delta m_\ell = 0, \pm 1$

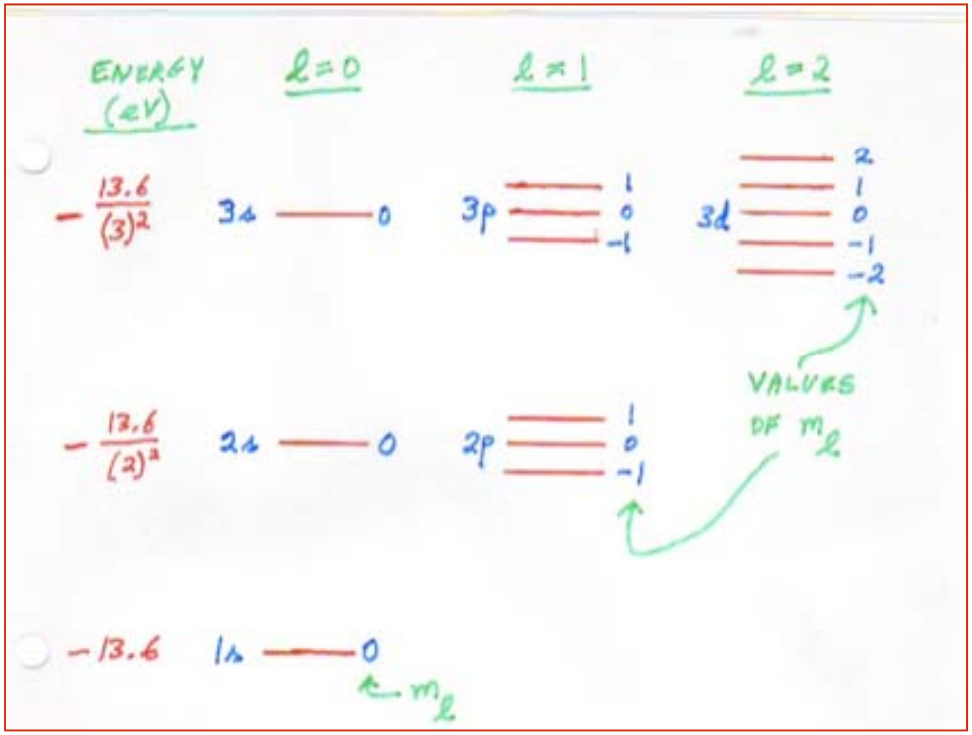
  This is called Selection Rules.

Energy Level Diagrams for Simple Hydrogen Model

B=0



B≠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), ~10^{-4} eV
  2. Electron-nucleon spin interaction (hyperfine structure): ~10^{-6} eV
  3. Quantum electrodynamics effect (Lamb shift): ~10^{-6} eV

  We will cover each of these briefly today.

Energy scales of each effect

$\alpha = \frac{e^2}{4\pi\varepsilon_0 \hbar c} \approx \frac{1}{137}$: Fine structure constant

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

Spin-Orbit Coupling

- The magnetic moments are:

$$\vec{\mu}_L = -g \frac{e}{2m} \vec{L} \qquad \text{with } g=1 \qquad (\text{orbit})$$

$$\vec{\mu}_S = -g \frac{e}{2m} \vec{S} \qquad \text{with } g \approx 2 \qquad (\text{spin})$$

- Interaction of μ_L and μ_S causes a ***fine-structure splitting*** of energy levels, even if $B_{external} = 0$!

Origin of Spin-Orbit Coupling

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

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

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

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

Thus

$$\Delta H = -\vec{\mu}_e \cdot \vec{B} \simeq -g\frac{e}{2m}\vec{S} \frac{\text{const}}{r^3} \vec{S} \cdot \vec{L}$$

Spin-Orbit effect, con't

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

$$E_{Dirac} = E_{Bohr}\left[1 + \frac{\alpha^2}{n}\left(\frac{1}{j+1/2} - \frac{3}{4n}\right)\right]$$

This result is obtained by Dirac.

Here, j is the total angular momentum quantum number corresponding to $\vec{J} = \vec{L} + \vec{S}$

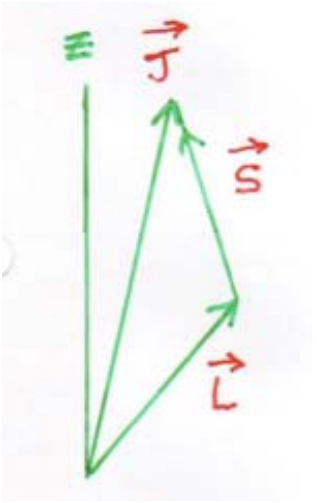
Spin-Orbit Coupling, con't

- "Vector model" of angular momentum:
  - Total angular momentum is:

$$\vec{J} = \vec{L} + \vec{S}$$

$$J = |\vec{J}| = \sqrt{j(j+1)}\,\hbar$$

$$J_z = m_j \hbar$$



  - Now we have
    - Total angular momentum quantum number j
    - Total magnetic quantum number m_j

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

$$m_j = -j, -j+1, \ldots +j$$

Dirac Theory: use n, ℓ, j, m_j
Instead of: n, ℓ, m_ℓ, m_s

Angular momentum Addition

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

If $\vec{J} = \vec{L}_1 + \vec{L}_2$ with $\vec{L}_1 \leftrightarrow l_1, m_{l_1}$, $\vec{L}_2 \leftrightarrow l_2, m_{l_2}$, $\vec{J} \leftrightarrow j, m_j$

$$j = |l_1 - l_2|, |l_1 - l_2| + 1, \cdots, l_1 + l_2$$

$$m_j = m_{l_1} + m_{l_2}$$

Hydrogen Fine-Structure

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

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

$$j = |\ell - 1/2| \text{ or } (\ell + 1/2)$$

- ***Most of the Schrodinger energy levels in Hydrogen should split into two levels***
- Exception: for ℓ=0, note j=1/2 only, so no splitting of ℓ=0 states.

Hydrogen Fine-Structure, con't

- The Bohr energy levels are:

$$E_{Bohr} = -\frac{13.6\,eV}{n^2} = -\left(\frac{1}{2}\alpha^2 mc^2\right)\frac{1}{n^2}$$

(order $\alpha^2 mc^2$)

- Recall the fine-structure constant: $\alpha = \frac{e^2}{4\pi\epsilon_0 \hbar c} \approx \frac{1}{137}$

- Now, in the Dirac theory:

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

$$\Rightarrow \Delta H = \sim \alpha^2 E_{Bohr} : \text{order } \alpha^4 mc^2$$

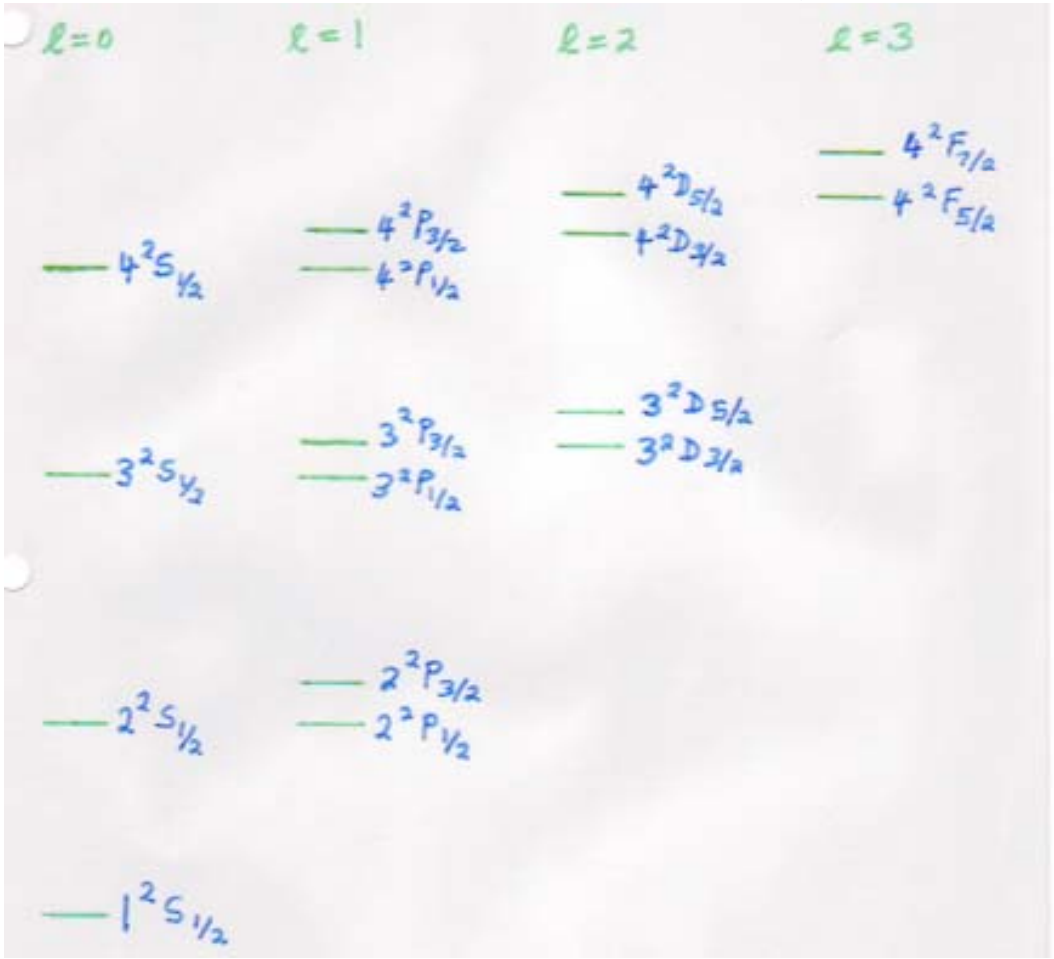
- In Schrodinger (and Bohr) theory, levels of the same n are degenerate.
- In the Dirac theory, levels of the same n and j are degenerate.

Spectroscopic Notation

- For each energy level: $n^{2s+1}L_j$
- Since s=1/2 in Hydrogen, 2s+1=2 always.
- Example:
  - n=4, ℓ=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 $B_{external}=0$

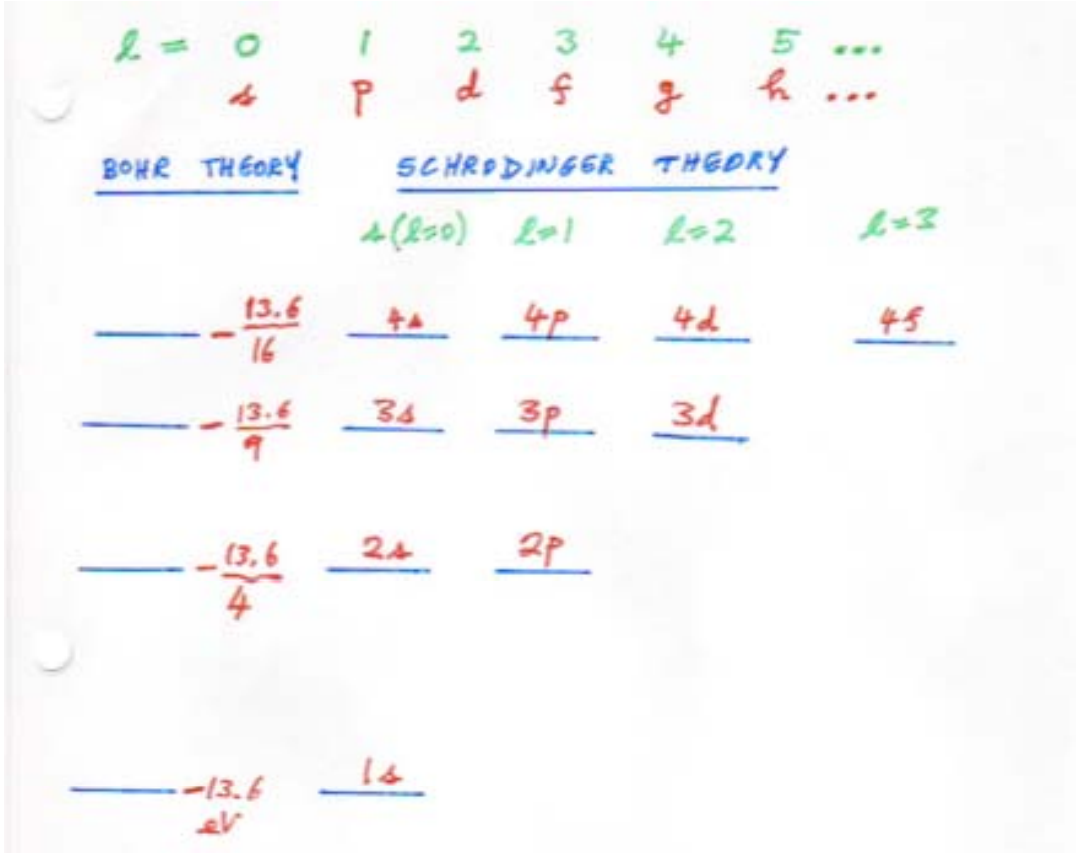


Notes:

1. **Clearly this is not to scale!**
2. **Levels of the same n and j are degenerate**
3. **S states (ℓ=0) are labeled "doublet" even though they are not!**

Compare to Bohr/Shrodinger theory

$B_{external} = 0$



Example

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

$$\Delta E_{FS} = E_{Bohr}\left[\frac{\alpha^2}{n}\left(\frac{1}{j+\frac{1}{2}} - \frac{3}{4n}\right)\right]$$

$$= -13.6\,eV\left[\left(\frac{1}{137}\right)^2\left(\frac{1}{1}\right)\left(\frac{1}{\frac{1}{2}+\frac{1}{2}} - \frac{3}{4(1)}\right)\right]$$

$$= -13.6\,eV\left[\left(\frac{1}{137}\right)^2\left(\frac{1}{4}\right)\right]$$

$$= -13.6\,eV\,(1.33\times10^{-5})$$

$$= -1.81\times10^{-4}\,eV$$

- A little below the Bohr value

Example

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

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

$$\Delta E_{FS}(j=1/2) = -(3.4\,eV)\left(\frac{1}{137}\right)^2\left(\frac{1}{2}\right)\left(\frac{1}{1/2+1/2} - \frac{3}{4.2}\right)$$

$$= -5.66\times10^{-5}\,eV$$

$$\Delta E_{FS}(j=3/2) = -(3.4\,eV)\left(\frac{1}{137}\right)^2\left(\frac{1}{2}\right)\left(\frac{1}{3/2+1/2} - \frac{3}{4.2}\right)$$

$$= -1.13\times10^{-5}\,eV$$

$$E(2^2P_{3/2}) - E(2^2P_{1/2}) = +4.53\times10^{-5}\,eV$$

- This is why it's called "fine" structure!

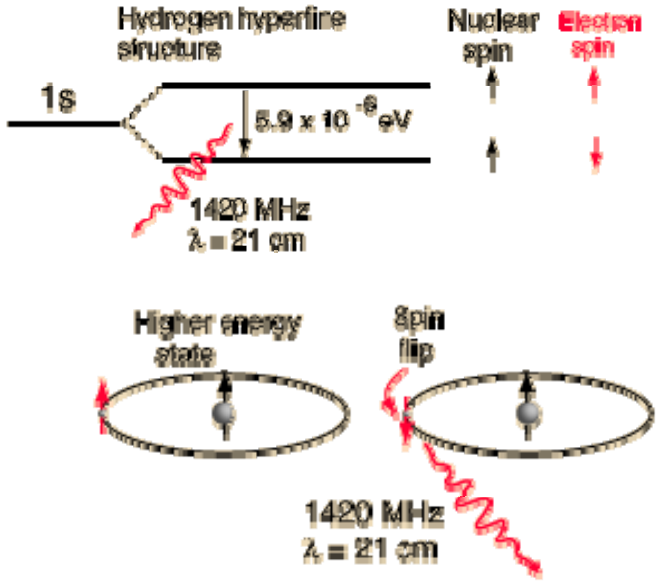
Hyperfine Structure

- Proton and neutrons are also spin 1/2 particles
- So nuclear spin angular momentum can interact with the electron's μ_J to split each Dirac energy level into two!
- But … it's a very tiny effect
  - Because $m_{proton} >> m_{electron}$

$$\text{“ } \vec{\mu} = g \frac{e}{2m} \vec{S} \text{ ”}$$

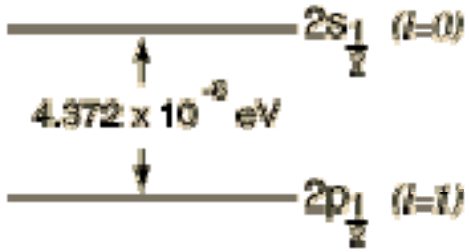
$$\Delta H = \sim (m/m_p)\, \alpha^4\, m\, c^2$$

- Hyperfine splitting is ~10^{-6} eV



There's even more to the story

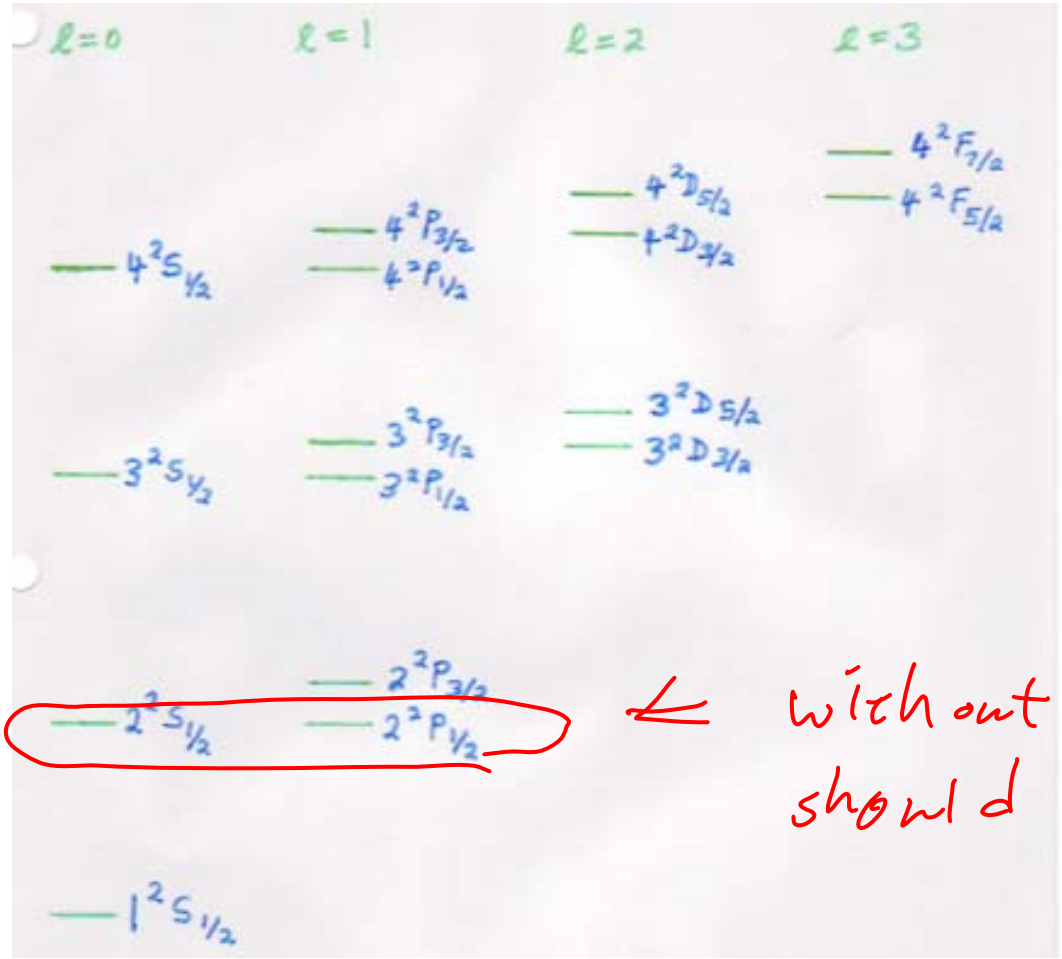
- In 1947, Willis Lamb discovered that the $2P_{1/2}$ state is slightly lower than the $2S_{1/2}$ state resulting in a slight shift of the corresponding spectral line
  - This is called the Lamb shift



- One would think that 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

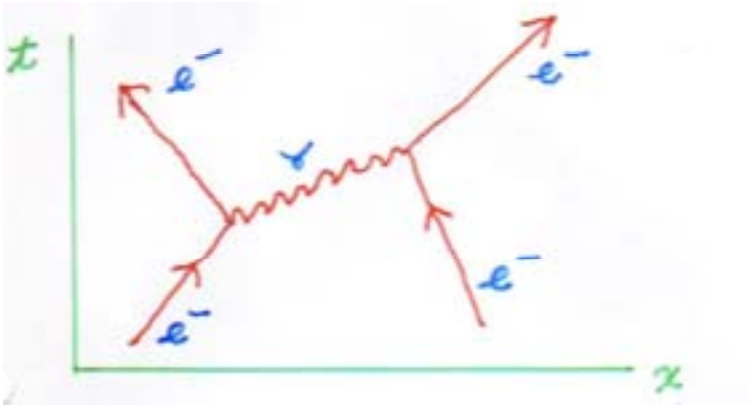
- Now in the Dirac theory with $B_{external}=0$



← without Lamb shift they should be equal.

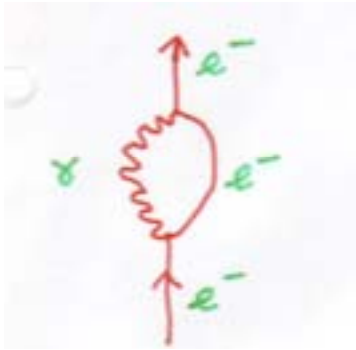
Quantum Electrodynamics (QED)

- Developed by Feynman, Schwinger, and Tomonaga in the 1940's
- The eletromagnetic 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



Electron emits and reabsorbs a virtual photon

Interactions with the "vacuum"

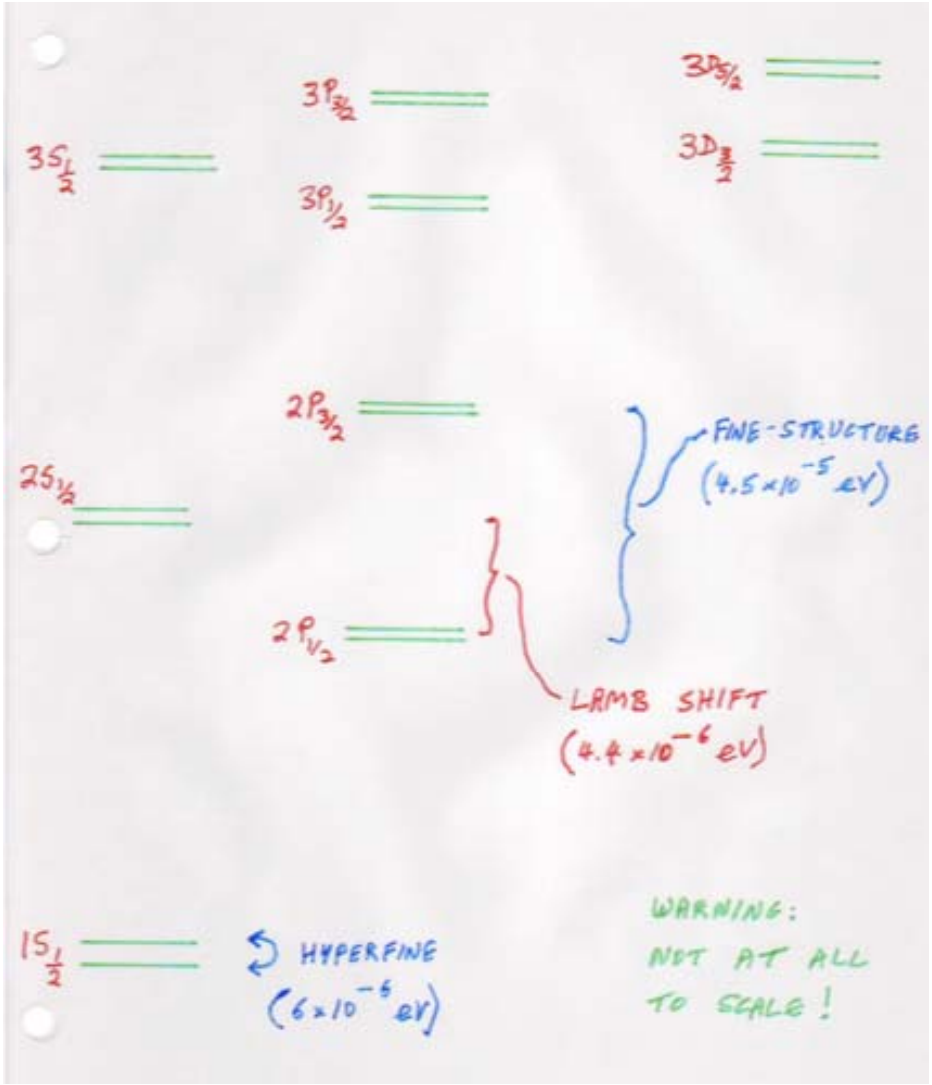
	QED Theory	Experiment
Electron's g factor	2.002319282 ±0.000000006	2.002319288 ±0.000000014
Fine-Structure $2P_{3/2}$-$2P_{1/2}$	1.096903×10^{10}Hz ±0.000004	1.096913×10^{10}Hz ±0.000010
Lamb Shift $2P_{1/2}$-$2S_{1/2}$	1.05791×10^{9}Hz ±0.00016	1.05790×10^{9}Hz ±0.00006
Hyperfine 21cm line	1.4204057×10^{9}Hz ±0.0000001	$1.4204057517864 \times 10^{9}$Hz ±0.00000000001

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



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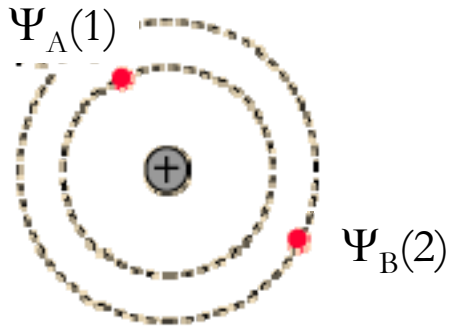
Multi-Electron Atoms

- 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:

$$(x_1, y_1, z_1) \qquad (x_2, y_2, z_2)$$

or

$$(\vec{r}_1) \qquad (\vec{r}_2)$$

- The total Hamiltonian operator for this system is

$$H_{op} = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 + V_{TOT}$$

- So the Schrodinger 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_{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,

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

or

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

- Note that the potential function is the same for both electrons

S.E. for Multi-electron atoms

$$-\frac{\hbar^2}{2m_1}\nabla^2\psi_{TOT} - \frac{\hbar^2}{2m_2}\nabla_2^2\psi_{TOT} + V_1\psi_{TOT} + V_2\psi_{TOT} = E_{TOT}\psi_{TOT}$$

- 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 Ψ will depend on quantum numbers

  n, ℓ, m_ℓ, 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:

$$\psi_{TOT} = \psi_A(1)\ \psi_B(2)$$

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

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_A\psi_B - \frac{\hbar^2}{2m_2}\nabla_2^2\psi_A\psi_B + V_1\psi_A\psi_B + V_2\psi_A\psi_B = E_{TOT}\psi_A\psi_B$$

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

- 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:

$$-\frac{\hbar^2}{2m_1}\nabla_1^2\psi_A + V_1\psi_A = E_A\psi_A$$

$$-\frac{\hbar^2}{2m_2}\nabla_2^2\psi_B + V_2\psi_B = E_B\psi_B$$

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

Exchange electrons

- So, we said that the total eigenfunction is:

$$\Psi_{TOT} = \psi_A(1)\,\psi_B(2)$$

- If we exchange electrons 1 and 2 we get:

$$\Psi_{TOT} = \psi_B(1)\,\psi_A(2)$$

- But the first equation gives:

$$\Psi_{TOT}^{*}\,\Psi_{TOT} = \psi_A^{*}(1)\,\psi_B^{*}(2)\,\psi_A(1)\,\psi_B(2)$$

- And the second (exchanged) equation gives:

$$\Psi_{TOT}^{*}\,\Psi_{TOT} = \psi_A^{*}(2)\,\psi_B^{*}(1)\,\psi_A(2)\,\psi_B(1)$$

- But these two probabilities are different!
  - This is not acceptable!
  - This means that the expressions for Ψ_{tot} above are not valid solutions!

Exchange electrons

- Since:

$$\psi^* \psi = |\psi|^2$$

- 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 Ψ_{Symm}
- - sign: Anitsymmetric eigenfunction Ψ_{Anti}

Symmetric and Antisymmetric

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

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

- Ψ_{Symm} and Ψ_{Anti} are degenerate!
  - Same energy
  - They exhibit "exchange degeneracy"
- They have the right properties:

$$\psi_{symm}(\text{after exchange}) = +\psi_{symm}(\text{before exchange})$$

$$\psi_{Anti}(\text{after exchange}) = -\psi_{Anti}(\text{before exchange})$$

- Note $1/\sqrt{2}$ is for normalization, assuming that Ψ_{tot} is normalized:

$$\int \psi_{symm}^{*}\psi_{symm}\,dx = \frac{1}{2}\left[\int \psi_{tot}^{*}\psi_{tot} + \int \psi_{tot}^{*}\psi_{tot}\right] = 1$$

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, ℓ, m_ℓ, m_s

Pauli Exclusion Principle

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

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

$$= \sqrt{2}\,\psi_A(1)\,\psi_A(2) \neq 0$$

  - So, Ψ_{Symm} permits 2 electrons in the same state.
  - So, Ψ_{Symm} violates the Pauli exclusion principle

$$\Psi_{Anti} = \frac{1}{\sqrt{2}}\left[\psi_A(1)\,\psi_A(2) - \psi_A(1)\,\psi_A(2)\right] = 0$$

- Ψ_{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

Required for Bosons

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

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