# Intermediate Quantum Mechanics <br> Lecture 20 Notes (4/8/15) 

The Hydrogen Atom III

## Degeneracy

- As noted in the last lecture, for a given value of $n$ the possible values of $l$ run from $l=0$ to $l=n-1$ and each of these different $l$ states have the same energy.

- Since for each $l$ value there are $2 l+1$ degenerate states, for a given $n$ the total degeneracy for a given $n$ is:

$$
\sum_{l=0}^{n-1}(2 l+1)=n^{2}
$$

## Electron Spin

- The electron carries an intrinsic angular momentum called spin. This angular momentum is given by the quantum number $s=1 / 2$. The possible values of the spin angular component along any axis (for example, the $z$-axis) is $m_{s} \hbar= \pm \hbar / 2$. The magnitude of the spin is $|\hat{\vec{s}}|=\sqrt{s(s+1)}=\sqrt{3} / 2$
- If there is no external magnetic field, $\hat{S}_{z}$ commutes with the Hamiltonian, $\left[\hat{H}, \hat{S}_{z}\right]$ and the energy is independent of the value of $m_{s}$. Since for each $n, l$ state there are two possible values of $m_{s}$, the degeneracy is increased by a factor of two. For a given value of $n$, the degeneracy is $2 n^{2}$.


## Total angular momentum

- The total angular momentum operator, $\hat{\vec{J}}$, is the vector sum of the orbital angular momentum operator and the spin angular momentum operator.

$$
\hat{\vec{J}}=\hat{\vec{L}}+\hat{\vec{S}} \quad \hat{J}_{z}=\hat{L}_{z}+\hat{S}_{z}
$$

- There are two values of $j$ depending upon whether the electron is spin-up or spin-down in the direction of $\vec{L}$. In the first case, we have: $j=l+1 / 2$. In the second case, we have: $j=l-1 / 2 . l=0$ is a special case with just one value of $j, j=1 / 2$.

$$
j= \begin{cases}l \pm 1 / 2 & l \neq 0 \\ 1 / 2 & l=0\end{cases}
$$

- For a state with given $n$ and $l$, there are two way of distinguishing the $n^{2}=$ $2(2 l+1)$ states. We can specify the quantum numbers $m_{l}$ and $m_{s}$ or we can specify the quantum numbers $j$ and $m_{j}$. Which set is the best to use, the so-called "good" quantum numbers, depends on the particular problem.
- For $l=1$ and $s=1 / 2$, the states are specified by either specifying the three values of $m_{l}$ times the two values of $m_{s}(3 \otimes 2)$ or by specifying the four values of $m_{j}$ for $j=3 / 2$ plus the two values of $m_{j}$ for $j=1 / 2(4 \oplus 2)$.


## Spin-orbit coupling

- For states with $l \neq 0$, there will be a coupling between the magnetic moment due to the orbital angular momentum and the the magnetic moment due to the spin angular momentum resulting in an energy shift.
- In the rest frame of the electron, the proton has an orbital angular momentum with respect to the electron that is equal to the orbital angular momentum of the electron with respect to the proton in the proton rest frame. In its rest frame, the electron sees a magnetic moment due to the proton orbital angular momentum. There will be a magnet dipole-dipole interaction between the magnetic moment due to the orbital angular momentum and the magnetic moment due to the electron spin.

$$
\begin{gathered}
\vec{\mu}_{L}=\frac{e}{2 m} \vec{L} \quad \vec{\mu}_{S}=-\frac{g e}{2 m} \vec{S} \\
\Delta E_{\mathrm{so}} \propto-\vec{\mu}_{L} \cdot \vec{\mu}_{S} \propto \vec{L} \cdot \vec{S}
\end{gathered}
$$

- $g$ is the gyromagnetic ratio for the electron. To first order, $g=2$ with a small $0.1 \%$ higher order correction. This value of $g=2$ follows directly from the relativistic Dirac equation.
- We can obtain an expression for $\vec{L} \cdot \vec{S}$ by the following:

$$
\begin{gathered}
J^{2}=\vec{J} \cdot \vec{J}=(\vec{L}+\vec{S}) \cdot(\vec{L}+\vec{S})=L^{2}+S^{2}+2 \vec{L} \cdot \vec{S} \\
\Rightarrow \quad 2 \vec{L} \cdot \vec{S}=J^{2}-L^{2}-S^{2} \quad \longrightarrow \quad j(j+1)-l(l+1)-3 / 4 \\
\Rightarrow \quad \Delta E_{\mathrm{so}} \propto(j+1)-l(l+1)-3 / 4
\end{gathered}
$$

- For the 2 p state we have:

| $\frac{2 \mathrm{p}_{j}}{2 \mathrm{p}_{1 / 2}}$ | $\frac{j}{1 / 2}$ | $\frac{l}{-}$ | $\frac{2 \vec{L} \cdot \vec{S}}{-2}$ |
| :--- | :--- | :--- | ---: |
| $2 \mathrm{p}_{3 / 2}$ | $3 / 2$ | 1 | 1 |

The four $j=3 / 2$ states are shifted up by one unit of energy while the two $j=1 / 2$ states are shifted down by two units of energy.


## Corrections to the hydrogen atom energy levels

- The following is a list all of the corrections to the energy levels of the hydrogen atom. The fractional size of the correction is given in parentheses.
- Reduced mass $\left(10^{-3}\right)$

The largest correction is to simply use the reduced mass instead of the electron mass:

$$
m_{\mathrm{red}}=\frac{m_{e} m_{p}}{m_{e}+m_{p}}=0.999 m_{e}
$$

It affects all of the energy levels equally.

- Relativistic energy-momentum relation $\left(10^{-5}\right)$

$$
\begin{aligned}
E=\sqrt{m^{2} c^{4}+p^{2} c^{2}} & =m c^{2} \sqrt{1+\frac{p^{2}}{m^{2} c^{2}}} \approx m c^{2}\left(1+\frac{p^{2}}{2 m^{2} c^{2}}-\frac{p^{4}}{8 m^{4} c^{4}}+\cdots\right) \\
& =m c^{2}+\frac{p^{2}}{2 m}-\frac{p^{4}}{8 m^{3} c^{2}}+\cdots
\end{aligned}
$$

Replace $\hat{H}=\frac{\hat{p^{2}}}{2 m}$ in the Schrodinger equation with $\hat{H}=\frac{\hat{p^{2}}}{2 m}-\frac{\hat{p^{4}}}{8 m^{3} c^{2}}$.

- Darwin term ( $10^{-5}$ )

The electron position is fuzzy by an amount equal to its Compton wavelength, $\hbar / m c=2.4 \times 10^{-12} \mathrm{~m}$. The electron can never be located more precisely than this. As a result, the electron does not experience a point source Coulomb potential but rather the source of the potential is smeared out by an amount equal to the Compton wavelength.

- Lamb shift $\left(10^{-6}\right)$

This is a quantum field theory correction. The first order Feynman diagram representing the Coulomb interaction between the electron and the proton in the hydrogen atom is the exchange of a virtual photon between the electron and the proton:


The next order corrections are given by the following diagrams in which the exchanged photon briefly turns into a virtual electron-positron pair or another virtual photon is exchanged between the initial and final electron. The first of these two diagrams is called vacuum polarization. Together the two diagrams give the Lamb shift. This is a slight (order of $10^{-6}$ shift of the $2 \mathrm{p}_{1 / 2}$ states to a lower energy than the $2 \mathrm{~s}_{1 / 2}$ states. This was predicted by Willis Lamb in the 1940's and shortly afterward experimentally confirmed. This successful prediction was an important step in establishing quantum field theory.


## - Finite size of the proton $\left(10^{-10}\right)$

This is an extremely small effect. The electron in the 1s state has a very small but non zero probability of being inside of the proton. It then experiences a Coulomb potential due to the effectively smaller proton charge.

