**Lecture 6 Highlights**

We began by recalling the energy level spectrum of the Hydrogen atom, $E_n = -13.6\,\text{eV}/n^2$, where $n = 1,2,3,4,...$ There are an infinite number of bound states of the proton and electron. Later we will study time-dependent perturbations that cause transitions between these 'stationary states.' When a hydrogen atom is excited to a higher energy level (e.g. by an electrical discharge in the gas), it can relax and give off light. The wavelengths of the emitted light are quantized as;

$$\frac{hc}{\lambda} = 13.6\text{ eV}\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right),$$

where $n_i$ is the initial (integer) n-value and $n_f$ is the final (integer) n-value for the transition.

We looked at the spectrum of Hydrogen with diffraction gratings. The results for the first few visible lines in the Balmer series of the H-atom are:

| **Balmer Series Line** | **Color** | **Observed λ (nm)** | **Calculated λ (nm)** |
|---|---|---|---|
| $H_\alpha$ | Red | 656.3 | 656.0 |
| $H_\beta$ | Turquoise / Cyan | 486.1 | 486.3 |
| $H_\gamma$ | Blue | 434.1 | 434.2 |

Not bad, but the differences between calculated and observed wavelengths are systematic errors. The theory of the H-atom is not complete!

The discrepancies are even greater when a magnetic field is applied to the Hydrogen atom. Classically, the electron orbiting the proton produces a current loop and therefore a magnetic moment $\vec{\mu}$ (which points anti-parallel to the angular momentum vector $\vec{L}$). In the presence of an external magnetic field $\vec{B}$, the Hydrogen atom takes on an additional contribution (perturbation) to its total energy, given by $H_{pert} = -\vec{\mu} \bullet \vec{B}$ (Griffiths, page 178). This is part of the Zeeman effect (Griffiths page 277), and it will split the degenerate (i.e. $\ell > 0$) energy levels of the Hydrogen atom into $2\ell+1$ states, depending upon the projection of $\vec{L}$ on $\vec{B}$. This in turn causes a splitting of the spectral lines, from a single line (in $\vec{B} = 0$) to $2\ell+1$ lines in finite field. Note that since $\ell$ is an integer or zero, $2\ell+1$ is always an odd integer. Indeed an odd number of spectral lines is often observed. However splitting into an even number of lines is also observed! (The Stern-Gerlach experiment was the first to show splitting into an even number of states in a magnetic field.) This cannot be explained by our current theory of the H-atom!

To resolve this problem Wolfgang Pauli suggested that a new quantum number was needed (beyond $n$, $\ell$, and $m$). He called this new property of the electron a "two-valuedness not describable classically." It was later thought to be due to the rotational motion of the electron on its axis, but Pauli showed this to be incorrect (you will too: HW2, problem 4.25). Nevertheless this property is now known as the "intrinsic spin angular momentum of the electron" and denoted by the 3D vector $\vec{S}$. It is an example of an N = 1 angular momentum ladder that we discussed in the last lecture. This gives rise to 2 values of a z-projection, and can explain the appearance of an even number of spectral lines in a magnetic field.

We postulate that the spin angular momentum has all of the same operators as orbital angular momentum:

$S^2$ operator with eigenvalues $s(s+1)\hbar^2$, $s = 1/2$ for the electron,

$S_z$ operator with eigenvalues $m_s\hbar$, with $m_s$ = -1/2 or +1/2.

The other operators are given on pages 171 and 172 of Griffiths. They obey commutation relations (and have uncertainty principles) analogous to those for orbital angular momentum. Note that there are $2s+1=2$ states in the ladder, and their z-component values are symmetric about zero, as expected for an angular momentum ladder. Because the internal degrees of freedom of the "spin angular momentum" are not accessible in 3D space (there are no 'spin-spherical-harmonics' that are functions of $\theta$ and $\phi$), we use the ket notation to describe the spin eigenstates: $\left| s \;\; m_s \right\rangle$. Spin states live in Hilbert space. For example the result of applying the spin raising and lowering operators ($S_\pm \equiv S_x \pm iS_y$) to the ket are:

$$S_\pm \left| s \;\; m_s \right\rangle = \hbar \sqrt{s(s+1) - m_s(m_s \pm 1)} \left| s \;\; m_s \pm 1 \right\rangle$$

Note that sometimes $m_s$ will be written simply as $m$ when it is clear from the context that it represents the $S_z$ eigenvalue.