Today we are going to study the selection rule of the Hydrogen atom. When excited above ground state, an electron will return to ground state and emit a photon. Transitions take place between energy states $|n,l,m\rangle$. The transition rule determines whether or not the transition is allowed between $|n,l,m\rangle$ and $|n',l',m'\rangle$. The emitted photon energy is equal to the difference in the energy of the two states $E_n - E_{n'} = \hbar\omega$.

Before we discuss this, we review what we already learned because it is important to understanding the selection rules. Do you remember angular momentum? We had these operators;

$$\hat{L}^2$$

$$\hat{L}_z$$

First we find the eigenvalue and the eigenfunction. The eigenfunctions are spherical harmonics.

$$\hat{L}^2 Y_l^m(\theta,\phi) = \hbar^2 l(l+1) Y_l^m(\theta,\phi)$$

$$\hat{L}_z Y_l^m(\theta,\phi) = \hbar m Y_l^m(\theta,\phi)$$

The details of these eigenfunctions can be written out as (these are the normalized spherical harmonics):

$$\boxed{Y_l^m(\theta,\phi) = \left[\frac{2l+1}{4\pi}\frac{(l-m)!}{(l+m)!}\right]^{1/2} P_l^m(\cos\theta) e^{im\phi}} \leftarrow \text{Memorize this!}$$

There are three recurrence relations for the associated Legendre Polynomials, we will use for understanding the transition rules (see page 375):

① $(2l+1)\cos\theta P_l^m(\cos\theta) = (l-m+1)P_{l+1}^m(\cos\theta) + (l+m)P_{l-1}^m(\cos\theta)$

② $(2l+1)\sin\theta P_l^m(\cos\theta) = P_{l-1}^{m+1}(\cos\theta) - P_{l+1}^{m+1}(\cos\theta)$

③ $\sin\theta P_l^m(\cos\theta) = (l-m)\cos\theta P_l^{m-1}(\cos\theta) - (l+m)P_{l-1}^{m-1}(\cos\theta)$

Also we need the associated Legendre orthogonality condition:

$$\int_0^\pi P_l^m P_k^m \sin\theta d\theta = \begin{cases} \frac{2}{2l+1}\frac{(l+m)!}{(l-m)!} & k = l \\ 0 & k \neq l \end{cases}$$

Next we review the Hydrogen atom. Before we solve the Hydrogen atom, we started with a two-body system. We found the eigenfunction like a plane wave with a relative Hamiltonian.

$$\hat{H} = \underbrace{\frac{\hat{p}_r^2}{2\mu} + \underbrace{\frac{\hat{L}^2}{2\mu r^2} - \frac{Ze^2}{r}}_{\text{Effective Potential}}}_{\text{Relative Hamiltonian for a hydrogenic atom of atomic number Z}}$$

$\leftarrow$ Here $-\frac{Ze^2}{r}$ is the Coloumb potential

Z is the central positive charge number

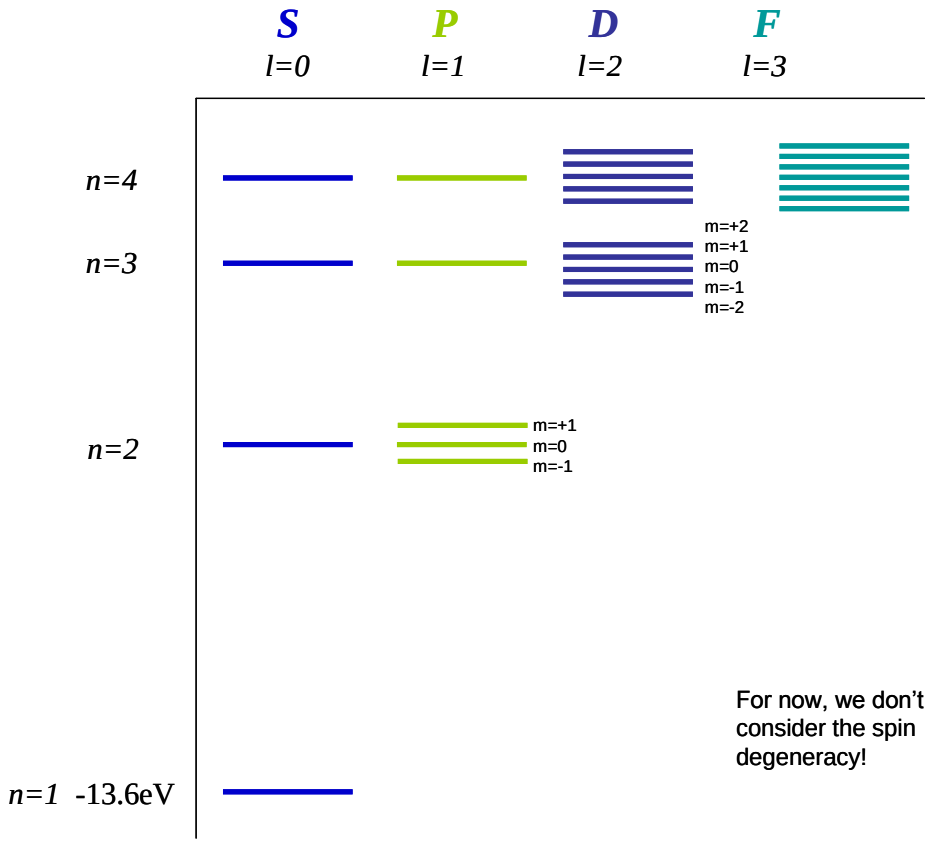
We can write the eigenfunctions this way:

$$\psi_{n,l,m} = R_{n,l}(r)Y_l^m(\theta,\phi)$$

and the eigenvalues this way (ground state at $n=1$):

$$E_n = -\frac{\mu\left(Ze^2\right)^2}{2\hbar^2 n^2}$$

You remember the energy diagram and the degeneracy of the energy values for a state $|n,l,m\rangle$.



Now we think classically. In classical mechanics, the electron orbits the positive nucleus and creates a dipole moment $P = er\cos(\omega t + \delta)$ where δ is the phase. But in classical mechanics, the electron will lose energy as it accelerates around and it will 'click' to the center.

In Quantum Mechanics, the physical variables change to operators:

$$\langle \gamma \rangle = \langle \varphi_n | \gamma | \varphi_n \rangle = \text{constant (time independent)}$$

So it is not like the classical dipole. For example:

$$\langle r \rangle = \langle \varphi_{nlm} | r | \varphi_{nlm} \rangle = 0$$

can't give light or radiation. The experiments show that the spectra of sunlight have higher to lower discrete transitions. Let's think about 2 energy levels:

$$|a|^2 = P(E_n) = \text{probability of } E_n \text{ existing}$$
$$|b|^2 = P(E_{n'}) = \text{probability of } E_{n'} \text{ existing}$$
$$|a|^2 + |b|^2 = 1$$
$$\psi = ae^{-E_n t/\hbar}\psi_n + be^{-E_{n'} t/\hbar}\psi_{n'}$$

Because here we only study the dipole approximation (quadrapole transitions are neglected), we write it this way: er.

$$\begin{aligned}
\langle r \rangle &= \langle \varphi_{nlm} | r | \varphi_{nlm} \rangle \\
&= \left\langle ae^{-E_n t/\hbar}\psi_n + be^{-E_{n'} t/\hbar}\psi_{n'} \middle| r \middle| ae^{-E_n t/\hbar}\psi_n + be^{-E_{n'} t/\hbar}\psi_{n'} \right\rangle \\
&= |a|^2 \cancelto{0}{\langle \psi_n | r | \psi_n \rangle} + |b|^2 \cancelto{0}{\langle \psi_{n'} | r | \psi_{n'} \rangle} \\
&\qquad + a^* b e^{(E_{n'} - E_n)t/\hbar} \langle \psi_n | r | \psi_{n'} \rangle + b^* a e^{(E_n - E_{n'})t/\hbar} \langle \psi_{n'} | r | \psi_n \rangle \\
&= a^* b e^{(E_{n'} - E_n)t/\hbar} \langle \psi_n | r | \psi_{n'} \rangle + b^* a e^{(E_n - E_{n'})t/\hbar} \langle \psi_{n'} | r | \psi_n \rangle \\
&\propto \underbrace{\langle \psi_n | r | \psi_{n'} \rangle \cos(\omega_{nn'} t + \delta)}_{\text{final results}}
\end{aligned}$$

Oscillation near the dipole $\hbar\omega_{nn'} = E_n - E_{n'}$. From the dipole relation, from theory $P = \frac{1}{3}\frac{\omega^4}{c^3}|d|^2$ where $d = er_0$ and $P = er_0\cos(\omega t + \delta)$. Actually we are only concerned about whether or not this is zero:

$$\langle \psi_n | r | \psi_{n'} \rangle \overset{?}{=} 0$$

$$\langle \psi_n | r | \psi_{n'} \rangle \begin{cases} = 0 & \text{transition is forbidden} \\ \neq 0 & \text{transition is allowed} \end{cases}$$

If it is non-zero, then a selection rule exists – the transition from $|n,l,m\rangle$ to $|n',l',m'\rangle$ exists.

The oscillation frequency is the energy difference divided by Planck's constant. I hope you can calculate that by yourself at home. There are several tricks for calculating the transition rules – here, we only select one of them. Start with:

$$r^2 = x^2 + y^2 + z^2 = \tfrac{1}{2}(x+iy)^2 + \tfrac{1}{2}(x-iy)^2 + z^2$$

Separate into components:

$\langle \psi_n | (x+iy) | \psi_{n'} \rangle$

$\langle \psi_n | (x-iy) | \psi_{n'} \rangle$

$\langle \psi_n | z | \psi_{n'} \rangle$

For simplicity, let's start with z. $z = r\cos\theta$.

$$\langle n | z | n' \rangle = \langle n | r\cos\theta | n' \rangle$$

$$= \int_{4\pi} d\Omega \cos\theta Y_l^m * Y_{l'}^{m'} \underbrace{\int_{-\infty}^{\infty} dr r^3 R_{nl}^*(r) R_{n'l'}(r)}_{\text{this term is non-zero so it can be disregarded in subsequent analysis}}$$

$$= \underbrace{\int_0^{\pi} \sin\theta d\theta P_l^m * (\cos\theta) \underbrace{\cos\theta P_{l'}^{m'}(\cos\theta)}_{\text{use equation ①}}}_{\substack{\text{write as } P_l^m\left(P_{l'+1}^{m'} + P_{l'-1}^{m'}\right) \text{ then use orthogonality condition equation ④} \\ \text{this is non-zero when: } l=l'+1 \text{ or when } l=l'-1}} \underbrace{\int_0^{2\pi} e^{i(m-m')\phi} d\phi}_{\substack{\text{this term is non-zero} \\ \text{when } m\text{-}m'=0 \text{ or} \\ \Delta m=0}}$$

$$\therefore \Delta l = \pm 1, \Delta m = 0$$

Now do another component

$$\langle n|x+iy|n'\rangle = \langle n|r\sin\theta e^{i\phi}|n'\rangle$$

$$= \int_{4\pi} d\Omega \sin\theta e^{i\phi} Y_l^m * Y_{l'}^{m'} \underbrace{\int_{-\infty}^{\infty} dr r^3 R_{nl}^*(r) R_{n'l'}(r)}_{\text{this term is non-zero so it can be disregarded in subsequent analysis}}$$

$$= \underbrace{\int_0^{\pi} \sin\theta d\theta P_l^m * (\cos\theta) \underbrace{\sin\theta P_{l'}^{m'}(\cos\theta)}_{\text{use equation ②}}}_{\text{write as } P_l^m\left(P_{l'+1}^{m'}+P_{l'-1}^{m'}\right) \text{ then use orthogonality condition equation ④; this is non-zero when: } l=l'+1 \text{ or when } l=l'-1} \underbrace{\int_0^{2\pi} e^{i(m-m'+1)\phi} d\phi}_{\text{this term is non-zero when } m-m'+1=0 \text{ or } \Delta m=1}$$

$$\therefore \Delta l = \pm 1, \Delta m = 1$$

You can do the same thing for the last component but use equation ③.

$$\langle n|x+iy|n'\rangle = \langle n|r\cos\theta e^{-i\phi}|n'\rangle$$

$$= \int_{4\pi} d\Omega \sin\theta e^{i\phi} Y_l^m * Y_{l'}^{m'} \underbrace{\int_{-\infty}^{\infty} dr r^3 R_{nl}^*(r) R_{n'l'}(r)}_{\text{this term is non-zero so it can be disregarded in subsequent analysis}}$$

$$= \underbrace{\int_0^{\pi} \sin\theta d\theta P_l^m * (\cos\theta) \underbrace{\cos\theta P_{l'}^{m'}(\cos\theta)}_{\text{use equation ①}}}_{\text{write as } P_l^m\left(P_{l'+1}^{m'}+P_{l'-1}^{m'}\right) \text{ then use orthogonality condition equation ④; this is non-zero when: } l=l'+1 \text{ or when } l=l'-1} \underbrace{\int_0^{2\pi} e^{i(m-m'-1)\phi} d\phi}_{\text{this term is non-zero when } m-m'-1=0 \text{ or } \Delta m=-1}$$

$$\therefore \Delta l = \pm 1, \Delta m = -1$$

To summarize:

$$\langle \psi_n | (x+iy) | \psi_{n'} \rangle \Rightarrow \Delta l = \pm 1, \Delta m = +1$$

$$\langle \psi_n | (x-iy) | \psi_{n'} \rangle \Rightarrow \Delta l = \pm 1, \Delta m = -1$$

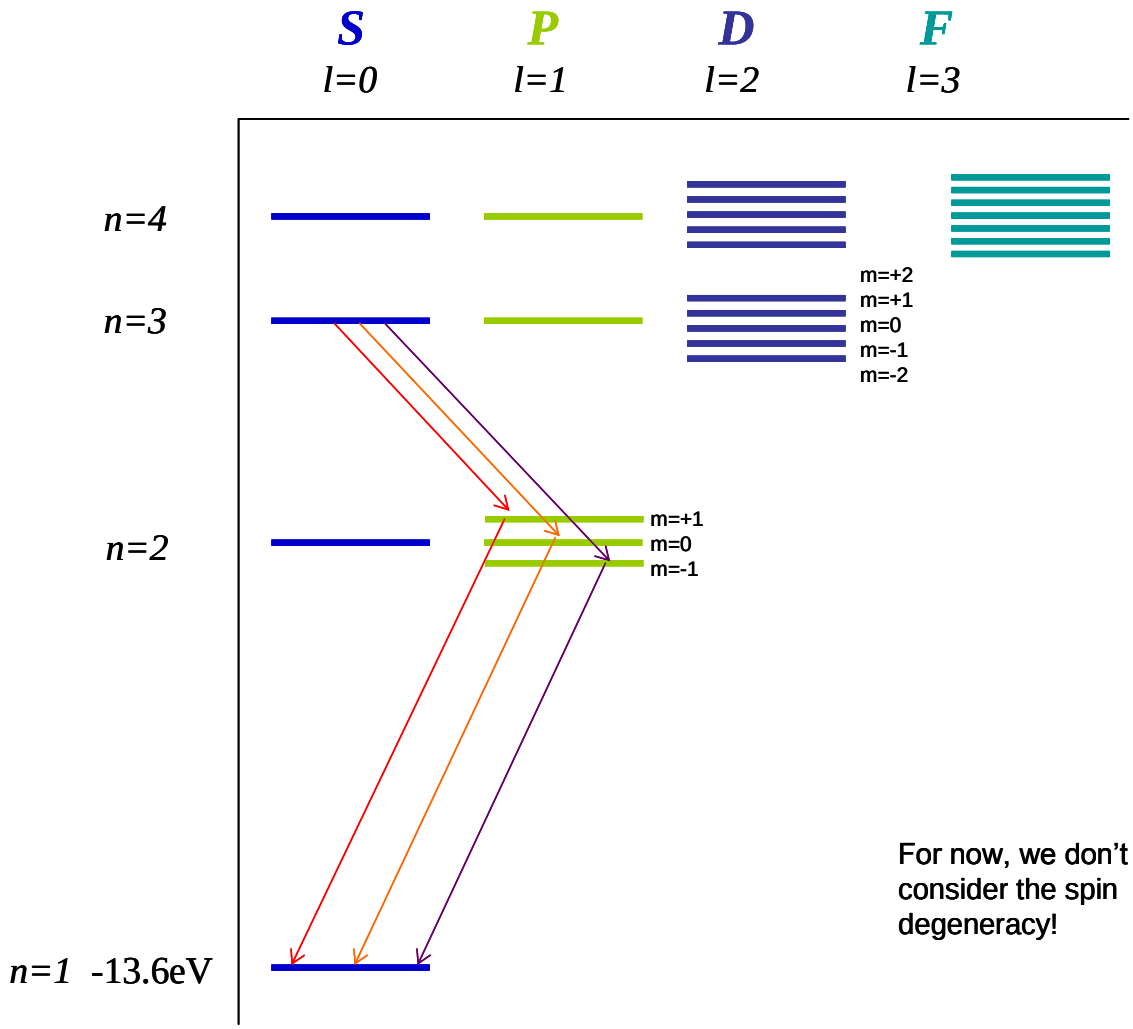
$$\langle \psi_n | z | \psi_{n'} \rangle \Rightarrow \Delta l = \pm 1, \Delta m = 0$$

$$\therefore \Delta l = \pm 1, \Delta m = 0, \pm 1$$

What we've shown is that we can use the recurrence relations of the associated Legendre polynomials to determine which transitions are allowed and which are forbidden. If you want to really calculate the real transition rate, you have to calculate it rigorously. Our derivation did not include the very weak quadrapole interactions; these can be neglected.

Example:
If the initial excited state is at $|n'=3, l'=0, m'=0\rangle = |3\ 0\ 0\rangle$, then how many ways can it return to ground state $|1\ 0\ 0\rangle$?
Answer:

$$|3\ 0\ 0\rangle \rightarrow \left| \begin{matrix} +1 \\ 2\ 1\ \ 0 \\ -1 \end{matrix} \right\rangle \rightarrow |1\ 0\ 0\rangle$$ There are three ways.



The angular conservation $\pm\hbar\omega$ is given to the photon. Every particle has spin. A boson has +1 spin. The spin is the rotation of the electron as it revolves around the nucleus – analogous to the rotation of Earth as it revolves around the Sun. The spin number of the electron is ½. In the next class we will learn about the spin, otherwise we can't go further. Spin interacts with the orbital angular momentum.

An important experiment: Stern-Gerlach (picture on page 524). The concept of spin explains the separation of a beam of electrons through a high gradient magnetic field.

Homework: 10.6