Spin related to spin and orbital magnetic moments, $\boldsymbol{\mu}_s$ and $\boldsymbol{\mu}_L$ of the H-atom:

$$\vec{\mu}_s = \gamma_s \vec{S} \qquad \vec{\mu}_L = \gamma_L \vec{L}$$

$$\vec{\mu}_{s_z} = \gamma_s \vec{S}_z \qquad \vec{\mu}_{L_Z} = \gamma_L \vec{L}_z$$

$$\gamma_s = -\frac{e}{m_e} \qquad \gamma_L = -\frac{e}{2m_e}$$

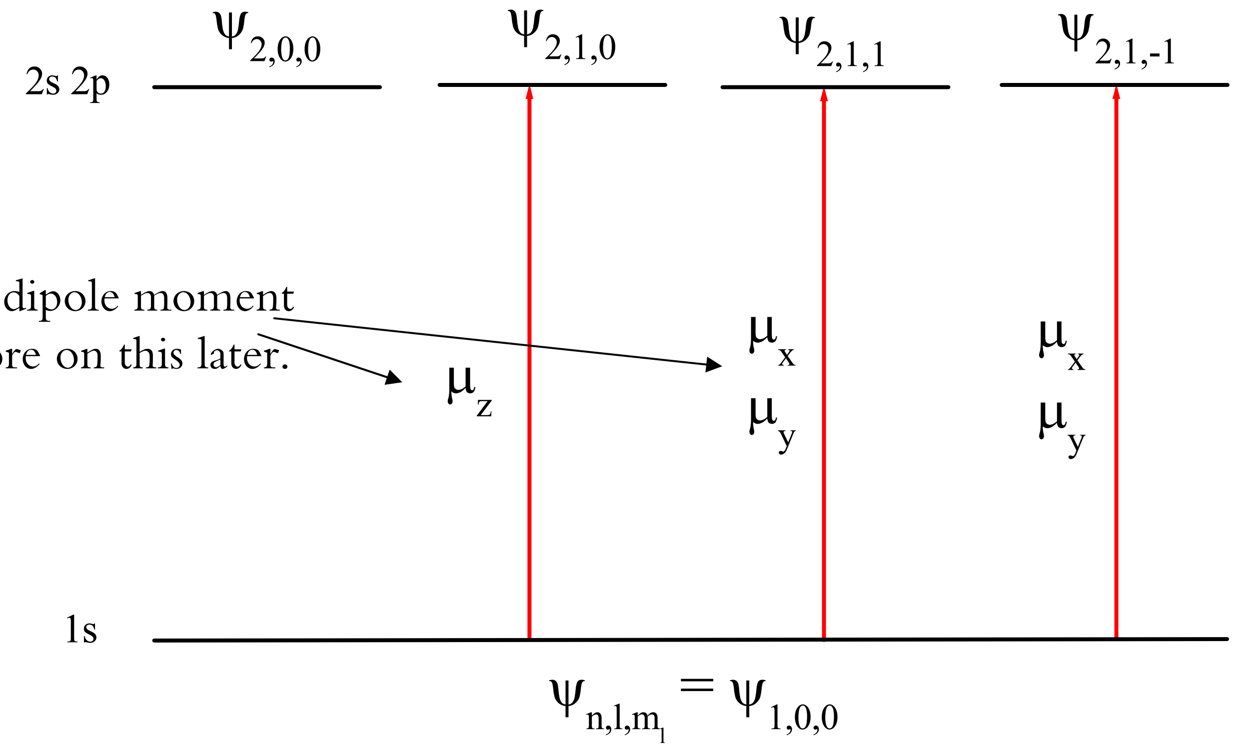
γ = "magnetogyric ratio" of the electron (having mass m_e) is a positive quantity since the charge on the electron is negative.

The quantity $\mu_B = \frac{|e|\hbar}{2m_e}$ has units of a magnetic dipole and is called a **Bohr magneton**.

$\mu_B = 9.274 \times 10^{-24}$ J T^{-1} in SI units

4.3: One electron atomic (Zeeman) spectroscopy

For a single electron problem (H-atom, Na atom, etc) we expect the following:



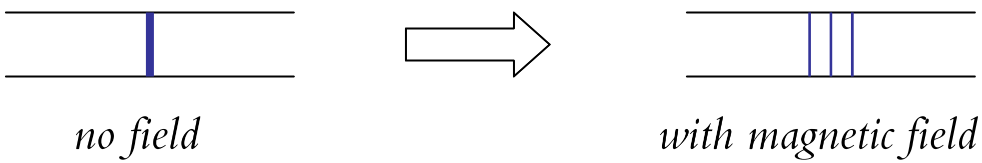
μ here is the dipole moment operator: More on this later.

Expect: 1 line (2s, 2p orbitals are degenerate) but see 3 lines.

The splitting in a magnetic field is called the **Zeeman effect**

The normal Zeeman effect (low magnetic field strengths) was observed in 1896

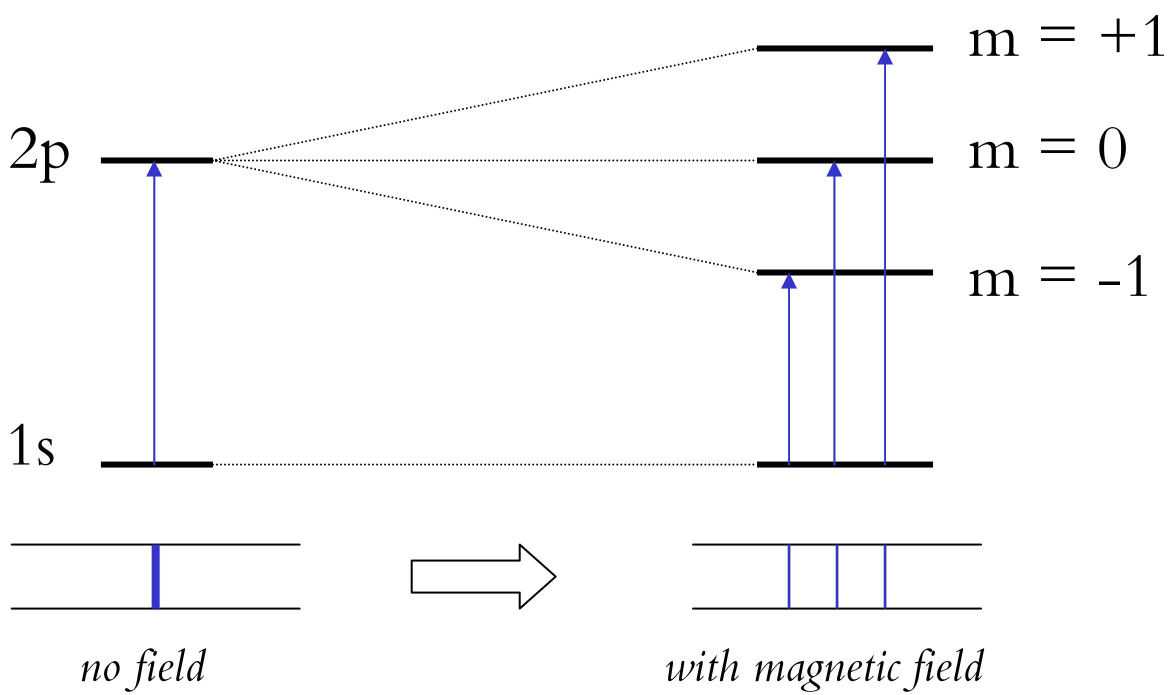
Experimentally, the atomic spectrum of hydrogen n=1 $\rightarrow$ n = 2 was modified by the application of a strong magnetic field. The normal Zeeman effect is the observation of three lines in the spectrum where, in the absence of the field, there was only one.



Recall that the atomic spectra result from transitions between energy levels. Somehow the application of the magnetic field changed a degenerate state into one of at least three different energy levels.

Explanation is that B-field removes the degeneracy since for l=1, m = -1, 0 or +1

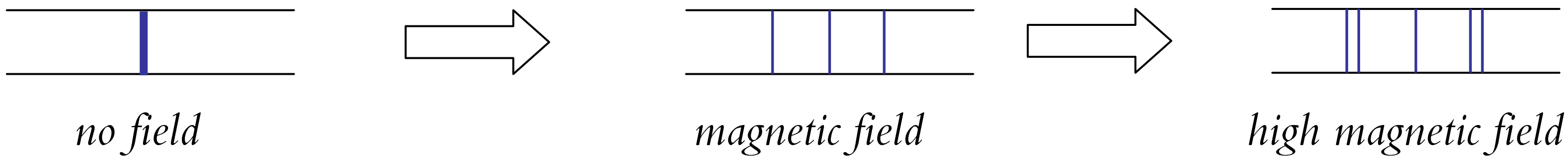
Thus, in the presence of a magnetic field states with the same principle quantum number n, do not necessarily have the same energy.



But wait: Nature is more interesting!

The Anomalous Zeeman Effect (not anomalous at all!)

In a very high magnetic field, the Zeeman triplet is found to be further split. This is known as the anomalous Zeeman effect.

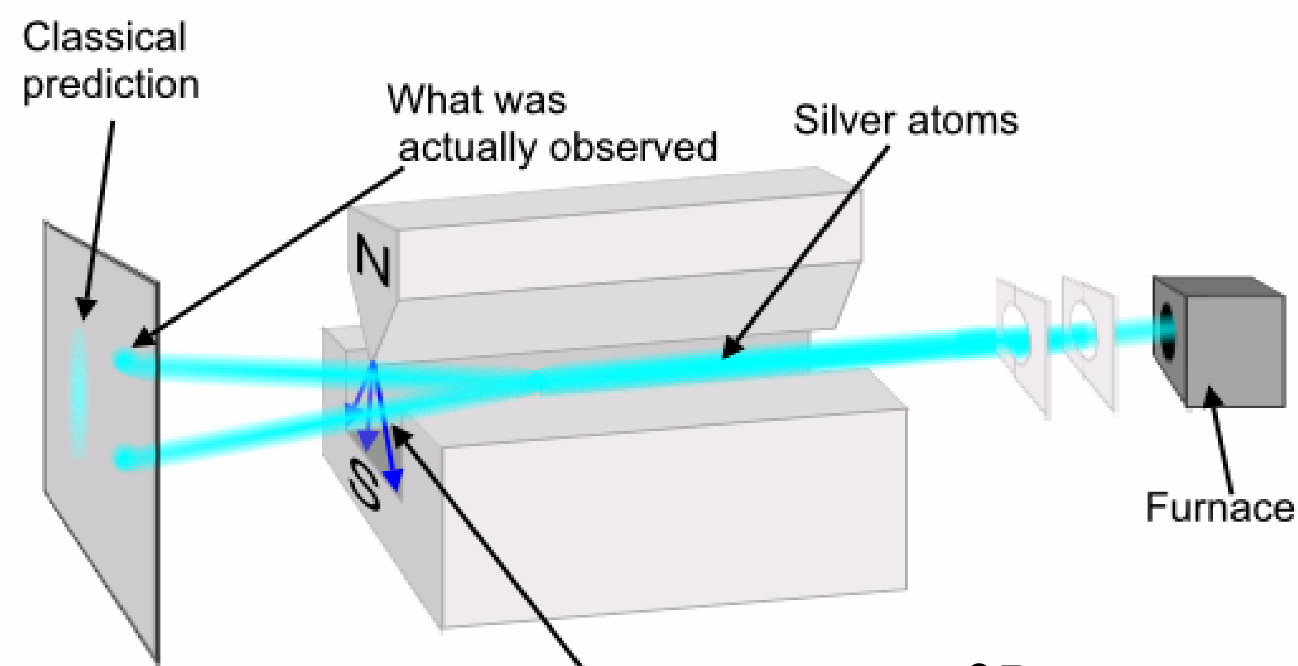


To explain this Goudsmit and Uhlenbeck in 1925 proposed that the electron has an intrinsic (built-in) magnetic moment independent of the orbital angular momentum. This intrinsic angular momentum results in a magnetic dipole moment that also interacts with an external magnetic field, resulting in the high field splitting.

The concept of electron spin was introduced. The spin of a particle is its intrinsic angular momentum (not due to its angular motion). The spin is a fixed characteristic of a particle, like its charge.

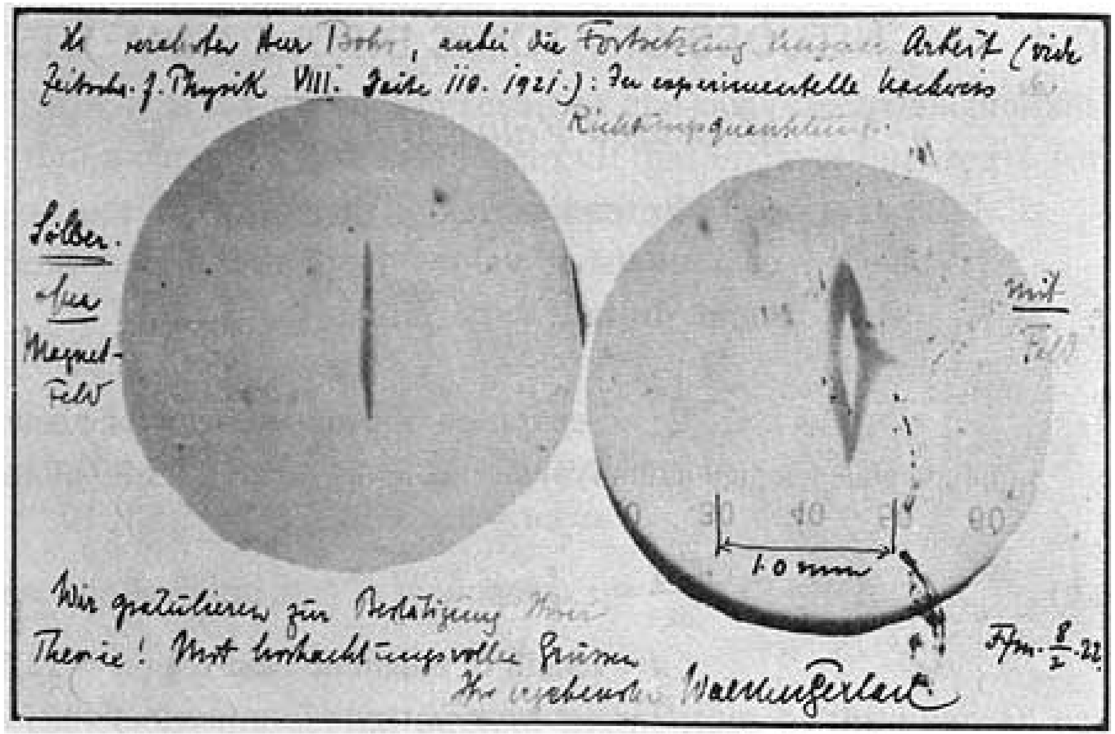
To a guarded extent, we can make an classical analogy that the electron is a sphere of charge spinning which results in an intrinsic angular momentum. This analogy is the origin of its name. However, spin is a purely quantum mechanical phenomenon without a true classical analogue.

Experimental verification of electron spin: **Stern-Gerlach experiment**



$$= \frac{\partial B}{\partial z}$$

Nobel Prize on a post card!



Gerlach's postcard, dated 8 February 1922, to Niels Bohr. It shows a photograph of the beam splitting, with the message, in translation: "Attached [is] the experimental proof of directional quantization. We congratulate [you] on the confirmation of your theory."

Postulate: 1-electron atoms possess a finite, intrinsic magnetic moment which interacts with the inhomogeneous field resulting in only **2** discrete values, and the effect is independent of the orbital motion of electron; that is, the effect is seen for H-atoms in 1s state.

The property behaves exactly like an angular momentum; responds to magnetic fields.

Spin Explanation

Atom has a magnetic moment which is due to the orbital motion of its electron **and** this new intrinsic property called (electron) spin.

$$\hat{\vec{\mu}}_m = \hat{\vec{\mu}}_\ell + \hat{\vec{\mu}}_s = \gamma_\ell \hat{L}_z + \gamma_s \hat{S}_z$$

$$= -\frac{\mu_B}{\hbar}\hat{L}_z - \frac{2\mu_B}{\hbar}\hat{S}_z = -\frac{\mu_B}{\hbar}\left(\hat{L}_z + 2\hat{S}_z\right)$$

$$\mu_B = \left|\frac{e\hbar}{2m_e}\right|$$ +ve quantity

Examine the experiment classically.

Interaction potential V in the inhomogeneous magnetic field is given by:

$$V = -\vec{\mu}_m \cdot \vec{B}$$

The resultant force F on the atom is given by:

$$\vec{F} = -\vec{\nabla} V = +\vec{\nabla}\left(\vec{\mu}_m \cdot \vec{B}\right)$$

If the inhomogeneous field is orientated in the z-direction

$$\vec{F} = \mu_{mz} \frac{\partial B}{\partial z} \hat{k}$$

Force along the z-direction will "bend" the beam if $\boldsymbol{\mu}_{mz} \neq 0$, and the direction of the bend will depend on the sign of the quantum numbers m_l and m_s

Consider H-atom with ψ_{n,ℓ,m_ℓ,m_s}

Then: $$\hat{\mu}_{mz}\psi_{n,\ell,m_\ell,m_s} = -\frac{\mu_B}{\hbar}\left(m_\ell\hbar + 2m_s\hbar\right)\psi_{n,\ell,m_\ell,m_s}$$
$$= -\mu_B\left(m_\ell + 2m_s\right)\psi_{n,\ell,m_\ell,m_s}$$

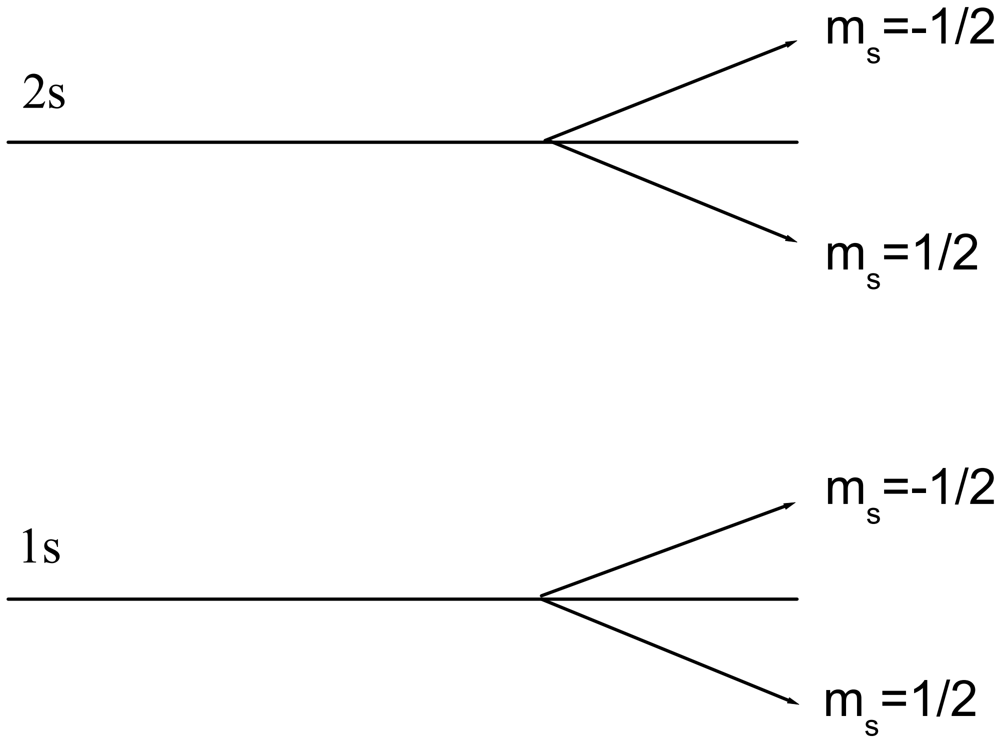
Hence the force in the z-direction $\mathbf{F}_z$ is given by:

$$\vec{F}_z = -\mu_B\left(m_\ell + 2m_s\right)\frac{\partial B}{\partial z}$$

Consider **1s** and **2s orbitals**:

$$n = 1 \quad \ell = 0 \quad m_\ell = 0 \quad s = \frac{1}{2} \quad m_s = \pm\frac{1}{2}$$

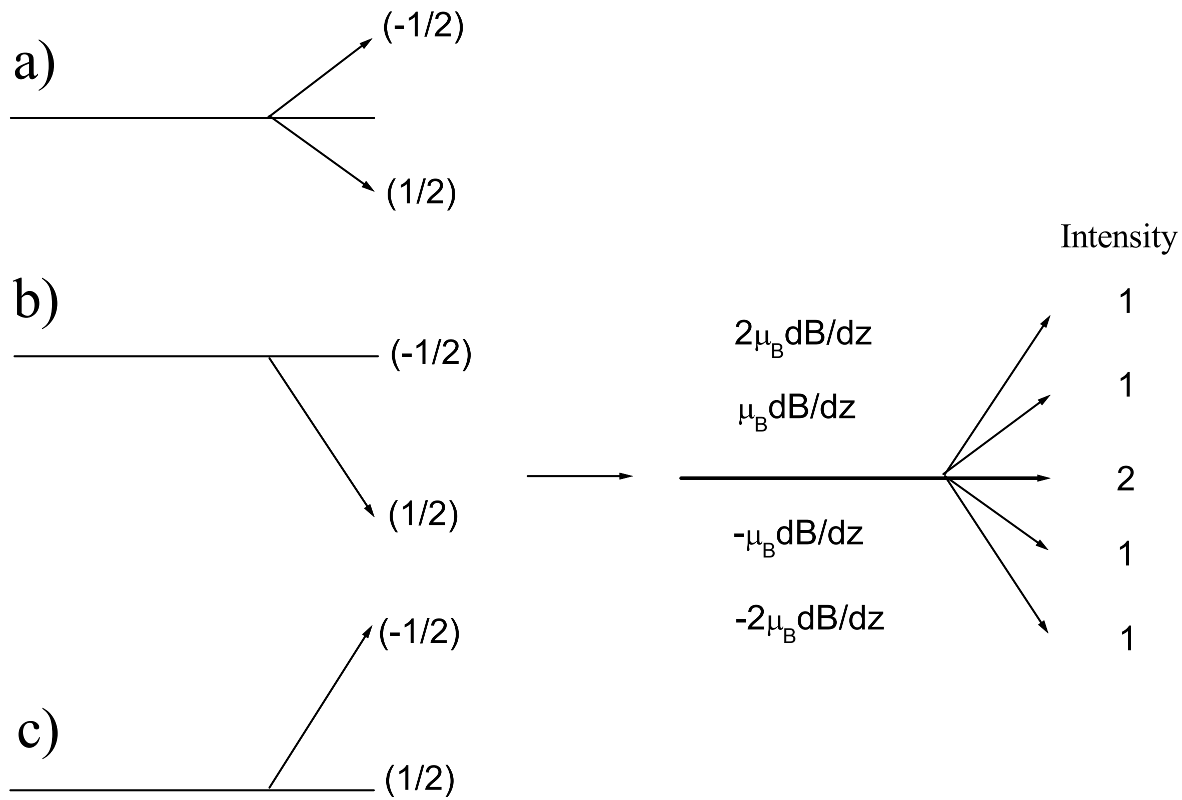
$$\therefore \vec{F}_z = -2\mu_B\left(\pm\frac{1}{2}\right)\frac{\partial B}{\partial z} = \mp\mu_B\frac{\partial B}{\partial z}$$



2s
m_s=-1/2
m_s=1/2
1s
m_s=-1/2
m_s=1/2

Consider **2p orbitals** $n = 2 \; \ell = 1$

	n	ℓ	m_ℓ	m_s	*deflection*
$a)$	2	1	0	$\pm\frac{1}{2}$	$\mp \mu_B \frac{\partial B}{\partial z}$
$b)$	2	1	1	$\pm\frac{1}{2}$	$-2\mu_B \frac{\partial B}{\partial z}, 0$
$c)$	2	1	-1	$\pm\frac{1}{2}$	$0, +2\mu_B \frac{\partial B}{\partial z}$



a)
(-1/2)
(1/2)
b)
(-1/2)
(1/2)
c)
(-1/2)
(1/2)
Intensity
$2\mu_B dB/dz$
$\mu_B dB/dz$
$-\mu_B dB/dz$
$-2\mu_B dB/dz$
1
1
2
1
1

The Zeeman effect with spin

For the H-atom, electric-dipole selection rules are:

$$\Delta \ell = \pm 1$$

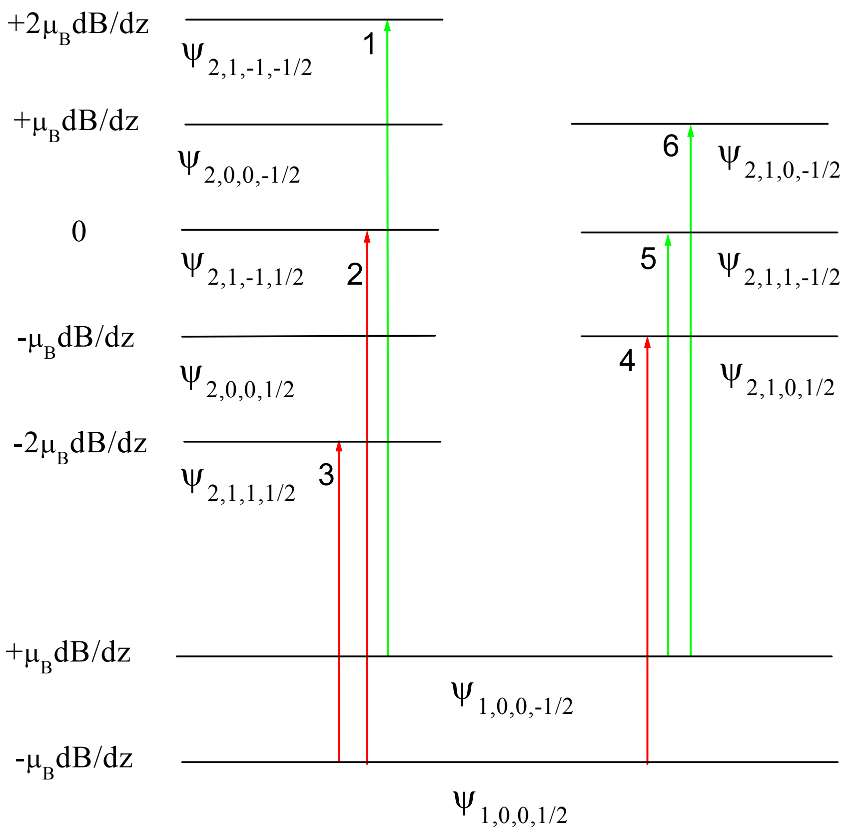
$$\Delta m_\ell = 0 \qquad \text{z-component of dipole moment}$$

$$\Delta m_\ell = \pm 1 \qquad \text{x- and y-components of dipole moment}$$

In addition: there is parity (even/oddness) of transition to consider:

$$\hat{\Pi}\psi_{n,\ell,m_\ell} = (-1)^\ell \psi_{n,\ell,m_\ell} \qquad \ell \text{ determines parity}$$

Lastly: $\Delta m_s = 0$ Electrons don't "flip" their spins during an electric-dipole transition.



Red lines originate from $\Psi_{1,0,0,1/2}$
Green lines originate from $\Psi_{1,0,0,-1/2}$
The colors are to only a visual aid.

Energy of transition 1 = transition 2
Energy of transition 3 = transition 5
Energy of transition 4 = transition 6

Therefore 6 allowed transitions yields 3 lines, each which is doubly degenerate because of the $\Delta m_s = 0$ requirement. Note: 1s →2s transition is forbidden

In reality see > 3 lines due to spin-orbit coupling. LATER