HYDROGEN IN MAGNETIC FIELD (ZEEMAN EFFECT)

Let us make a "classical mechanics" picture of the H atom. We have an immobile nucleus, around which an electron rotates, describing a closed loop (if it has orbital angular momentum).
The electron is charged and thus forms a closed current loop, which has an associated magnetic moment:

$$\mu = \underset{\substack{\uparrow \\ \text{current}}}{I} \cdot \underset{\substack{\uparrow \\ \text{area}}}{A} = \frac{-e v}{2\pi r} \cdot \pi r^2 = -\frac{e v r}{2} = -\frac{e}{2m} \overbrace{m v r}^{|\vec{L}|}$$

Let me now use the quantum mechanical $\vec{L}$ operator:

$$\mu = -\frac{e\hbar}{2m} \cdot \frac{|\vec{L}|}{\hbar}$$

$\frac{|\vec{L}|}{\hbar}$ is a number: $\sqrt{\ell(\ell+1)}$ (if calculated on eigenstate of L^2)

$\frac{e\hbar}{2m}$ is the BOHR MAGNETON $\mu_B = 5.8 \cdot 10^{-5}$ eV/T

This magnetic moment interacts with magnetic fields. Let us apply a magnetic field $\vec{B}$. The interaction between $\vec{\mu}$ and $\vec{B}$ will contribute the following term to the potential energy:

$$E = -\vec{\mu} \cdot \vec{B}$$

Let us take $\vec{B} = B_z \cdot \hat{z}$. Hence:

$$E = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z = +\frac{\mu_B}{\hbar} \cdot L_z \cdot B_z$$

goes after we show $\langle L_z \rangle = m\hbar$

States with the same quantum number n but different quantum number m (the z component of $\vec{L}$) will have different energy eigenvalues when immersed in a magnetic field $\vec{B}$: we broke the n^2 degeneracy

Let us take a small step back:

$$\vec{\mu} = -\mu_B \frac{\vec{L}}{\hbar}$$

I am interested in its z component, because I want to calculate the energy shift caused by a contribution:

$$E = -\mu_z B_z$$

Given an energy eigenstate of the Hamiltonian <u>without</u> $\vec{B}$ field $\psi_{n\ell m}(r,\theta,\varphi)$, I can calculate the energy shift:

$$\langle E \rangle = -\langle \mu_z \rangle B_z \qquad \text{where} \quad \langle \mu_z \rangle = -\mu_B \frac{\langle L_z \rangle}{\hbar}$$

What is $\langle L_z \rangle$? The conjugate coordinate of L_z is φ, hence:

$$L_z \longrightarrow \frac{\hbar}{i}\frac{\partial}{\partial\varphi}$$

Therefore:

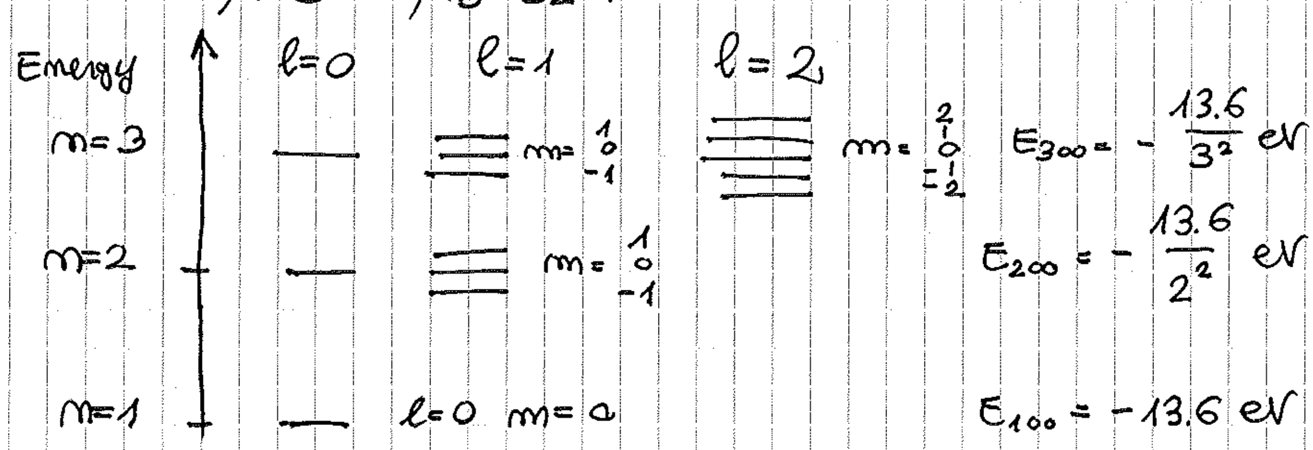
$$\langle \psi_{n\ell m}(r,\theta,\varphi) | L_z | \psi_{n\ell m}(r,\theta,\varphi) \rangle = \langle e^{-im\varphi} | \frac{\hbar}{i}\frac{\partial}{\partial\varphi} | e^{im\varphi} \rangle =$$

$$= m\hbar$$

$R_{n\ell}(r)$ and $\Theta_{\ell m}(\theta)$ commute with $\frac{\partial}{\partial\varphi}$ and are normalized

The Zeeman energy shift is thus:

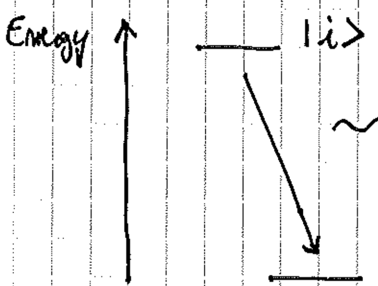
$$E = -\vec{\mu}\cdot\vec{B} = \mu_B \cdot B_z \cdot m$$



μ_B is $\sim 5.8 \cdot 10^{-5}$ eV/T. Maximum $\vec{B}$ field we can create is about 10T, so the Zeeman splitting is rather small compared to the Rydberg energy scale $-\frac{13.6}{n^2}$ eV

However, what we can observe is not the Energy spectrum, but energy differences of radiative transitions.

Let us model a transition from an initial state $|i\rangle$ and a final state $|f\rangle$:



$$|i\rangle = \psi_{nlm} \cdot e^{-iE_n t/\hbar}$$

irradiated photon: $e^{i\vec{k}\cdot\vec{r}}$ $\quad K = \dfrac{E_n - E_{n'}}{\hbar c}$

$$|f\rangle = \psi_{n'l'm'} \, e^{-iE_{n'} t/\hbar}$$

this is DIPOLE APPROXIMATION

It can be shown that the radiative transition probability is proportional to:

$\langle f | -e\vec{r} | i \rangle$ = expectation value of electric dipole moment of atom when doing transition from $|i\rangle$ to $|f\rangle$

Let us calculate this quantity:

$$\langle f | -e\vec{r} | i \rangle = -e \int \psi^*_{n'l'm'} \, e^{iE_{n'} t/\hbar} \cdot \vec{r} \, \psi_{nlm} \, e^{-iE_n t/\hbar} \, d^3\vec{r} =$$

$$= -e \int \psi^*_{n'l'm'} \, \psi_{nlm} \, e^{-i\omega t} \, \vec{r} \, d^3\vec{r}$$

where $\omega = \dfrac{E_n - E_{n'}}{\hbar}$. Unless the integral is identically 0,

I will have a time-oscillating dipole ($\propto e^{-i\omega t}$) which will emit photons

Let us go into Cartesian coordinates, and check what happens with the azimuthal angle φ:

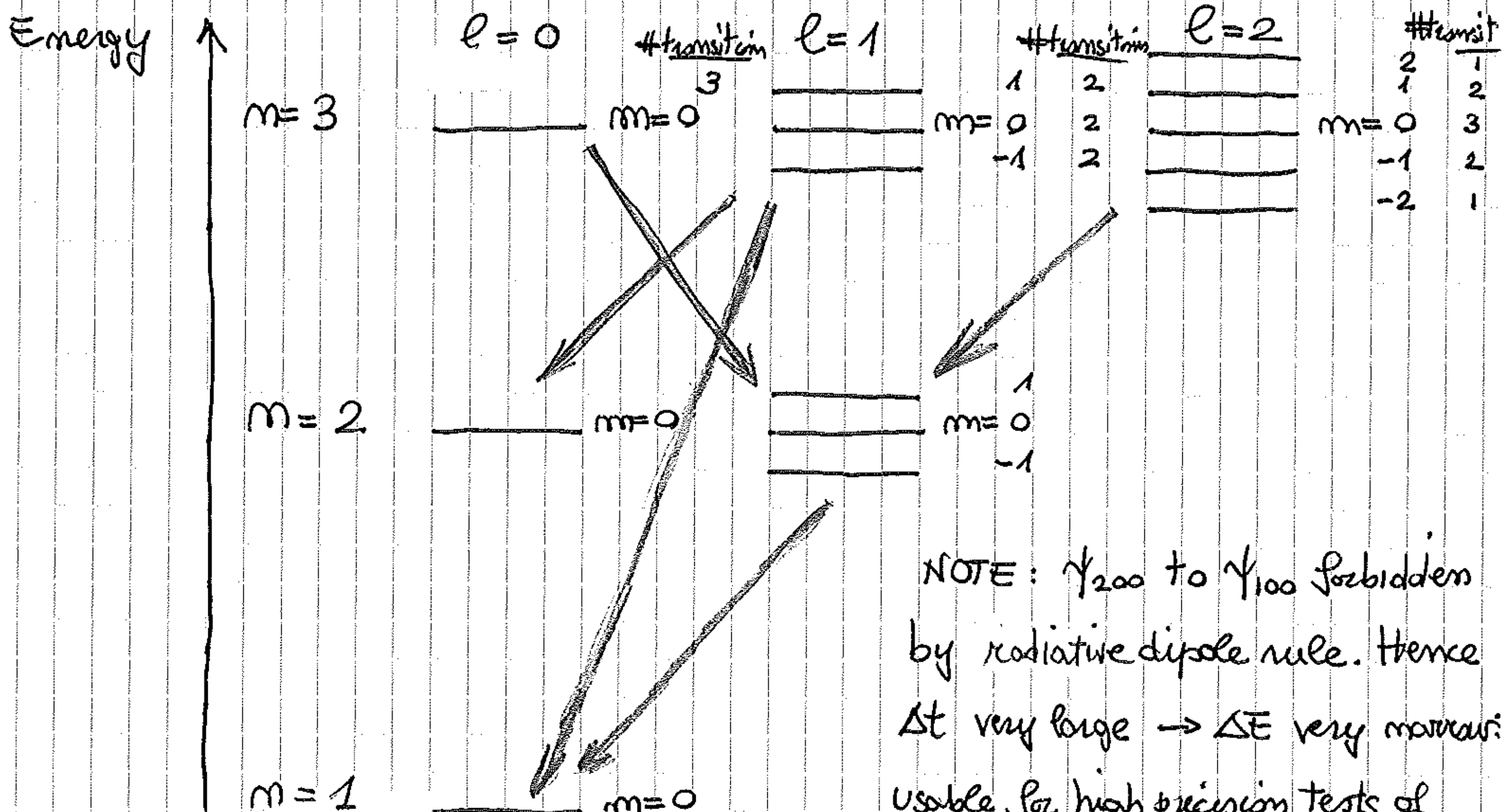
$$\vec{r} = \begin{cases} r\sin\vartheta\cos\varphi & \hat{x} \\ r\sin\vartheta\sin\varphi & \hat{y} \\ r\cos\vartheta & \hat{z} \end{cases} \qquad \begin{aligned} \psi_{n\ell m}(r,\vartheta,\varphi) &\propto e^{-im\varphi} \\ \psi_{n'\ell' m'}(r,\vartheta,\varphi) &\propto e^{-im'\varphi} \end{aligned}$$

$$\hat{z} \propto \int_0^{2\pi} d\varphi \; e^{im'\varphi} \cdot e^{-im\varphi} = \underline{\underline{0}} \text{ unless } m' = m$$

$$\hat{x}, \hat{y} \propto \int_0^{2\pi} d\varphi \; e^{im'\varphi}\left(\frac{e^{i\varphi} \pm e^{-i\varphi}}{2(i)}\right) e^{-im\varphi} \Rightarrow \int_0^{2\pi} d\varphi \; e^{i(m' \pm 1 - m)} = 0$$

unless $m' = m \mp 1$

Some (not all!) of these integrals can be $\neq 0$ if $\Delta m = 0, \pm 1$.
Similarly, if I repeat the exercise with the ϑ part, I get $\Delta \ell = \pm 1$
Finally, here is a map of the allowed radiative transitions (in dipole approximation):



NOTE: ψ_{200} to ψ_{100} forbidden by radiative dipole rule. Hence Δt very large $\rightarrow \Delta E$ very narrow: usable for high precision tests of quantum electrodynamics