Electronic dipole transitions

$$\varphi_{n\ell m} \longrightarrow \varphi_{n'\ell'm'} \qquad (\text{initial} \to \text{final})$$

During transition, electron is in superposition state

$$\Psi \propto \varphi_{n\ell m}\, e^{-i\frac{E_n}{\hbar}t} + \varphi_{n'\ell'm'}\, e^{-i\frac{E_{n'}}{\hbar}t}$$

This has a dipole moment

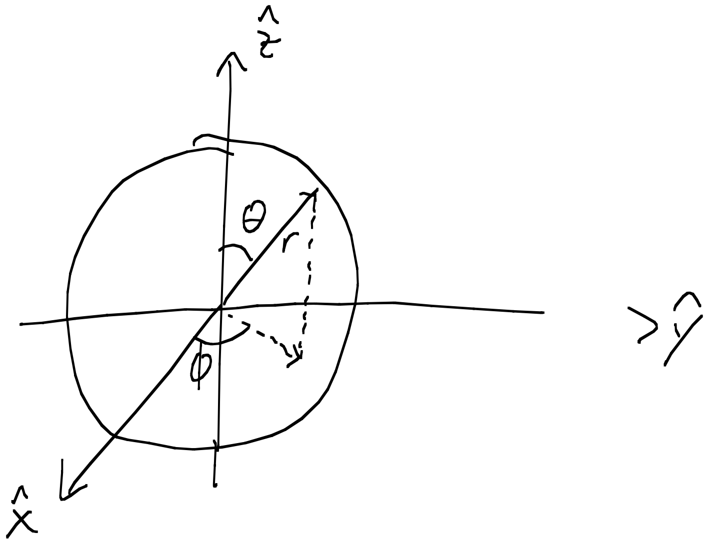
$$-e\langle \vec{r} \rangle = -e \langle \Psi | \vec{r} | \Psi \rangle$$

$$= -e \int \vec{r} \left\{ |\varphi_{n\ell m}|^2 + |\varphi_{n'\ell'm'}|^2 + \varphi^*_{n'\ell'm} \varphi_{n\ell m} e^{-i\omega t} + \varphi^*_{n\ell m} \varphi_{n'\ell'm'} e^{+i\omega t} \right\} d^3\vec{r}$$

$$= -e \int \vec{r} \left\{ \varphi^*_{n'\ell'm'} \varphi_{n\ell m} e^{-i\omega t} + \varphi^*_{n\ell m} \varphi_{n'\ell'm'} e^{+i\omega t} \right\} d^3\vec{r} \qquad \left(\omega \equiv \frac{E_n - E_{n'}}{\hbar} \right)$$

Selection Rules

$$\vec{r} = \begin{cases} r\sin\theta\cos\phi & \hat{x} \\ r\sin\theta\sin\phi & \hat{y} \\ r\cos\theta & \hat{z} \end{cases}$$



Vector components of ϕ integral:

$$\hat{x},\hat{y} \quad \propto \int_0^{2\pi} e^{-im'\phi}\left[\frac{e^{i\phi} \pm e^{-i\phi}}{2(i)}\right] e^{im\phi}\, d\phi \longrightarrow \int_0^{2\pi} e^{i(-m'\pm 1+m)\phi}\, d\phi = 0$$

<u>unless</u> $m - m' = \pm 1$

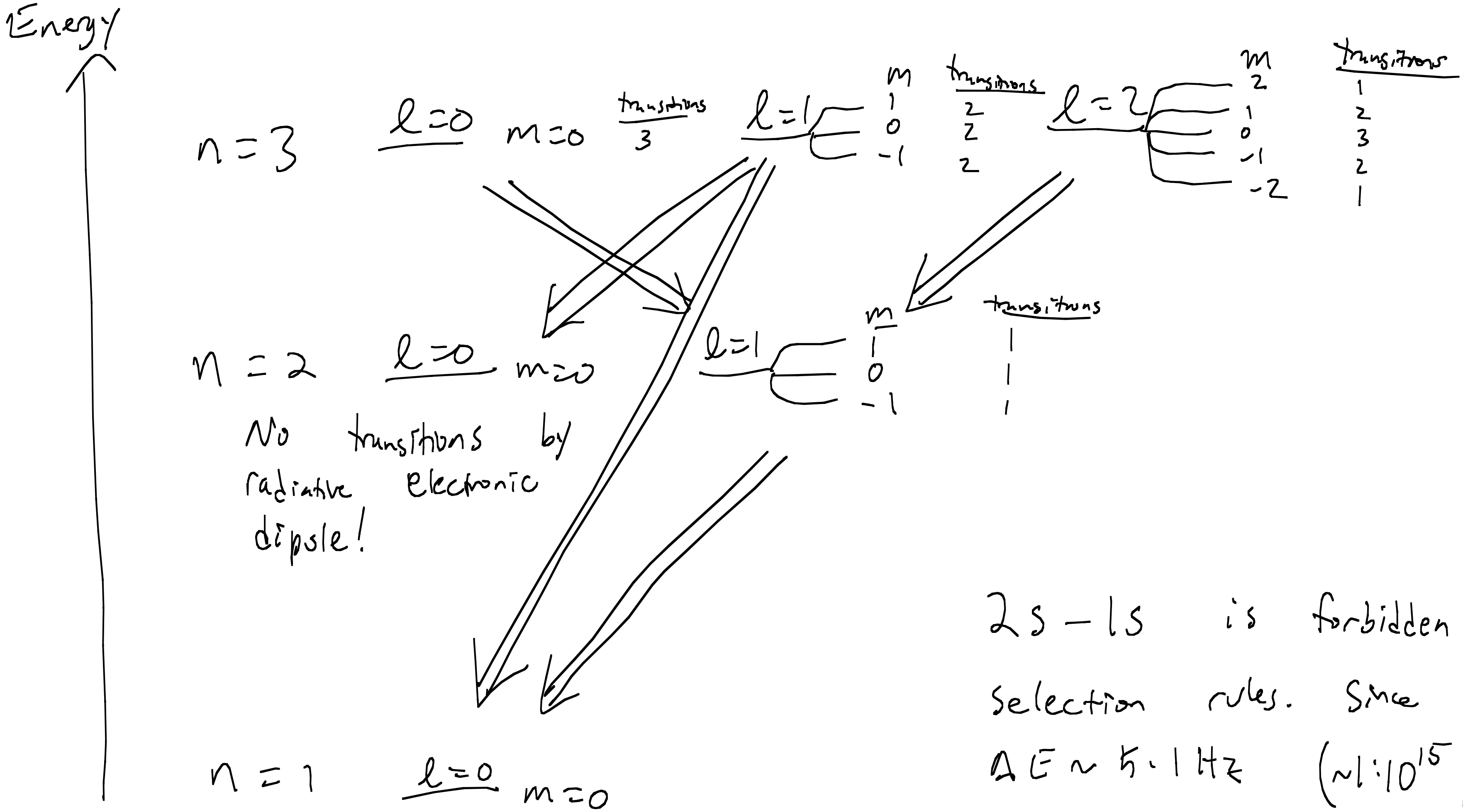
$$\hat{z} \quad \propto \int_0^{2\pi} e^{-im'\phi}\, e^{im\phi}\, d\phi = 0$$ <u>unless</u> $m - m' = 0$

Only transitions allowed have $\Delta m = 0, \pm 1$

Also (without proof): $\Delta l = \pm 1$ (from θ integral)

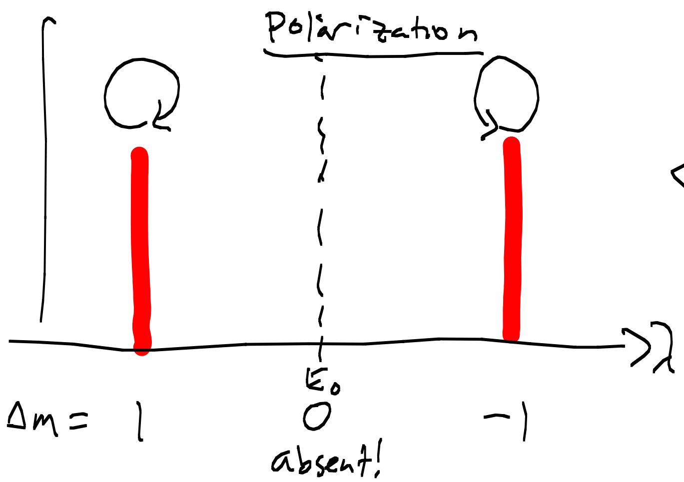
"Normal Zeeman effect": Allowed transitions

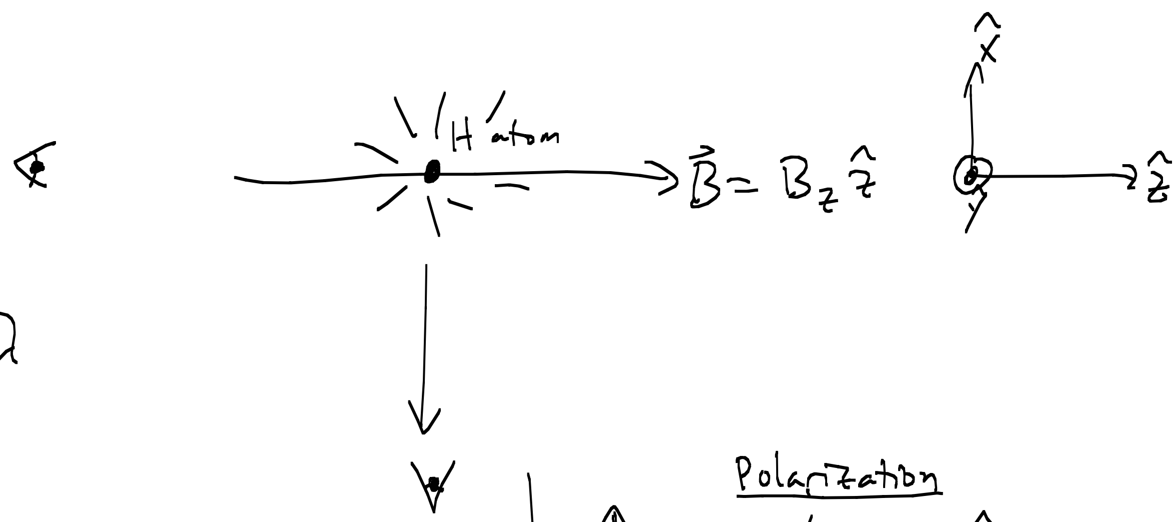
Only $\Delta \ell = \pm 1$, $\Delta m = 0, \pm 1$ $\longrightarrow$ each line splits into a triplet!

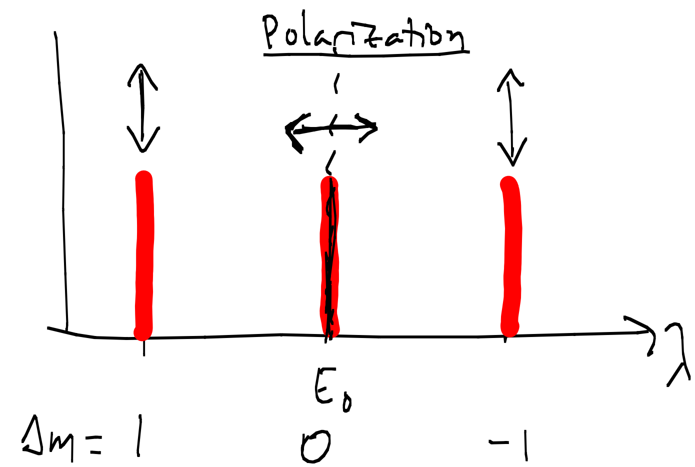


2s – 1s is forbidden by selection rules. Since Δt large, $\Delta E \sim 5.1$ Hz ($\sim 1:10^{15}$ precision!)

Polarization of Radiative transitions ("Normal" Zeeman Effect)







All properties can be derived from the electric dipole vector components but Lorentz used classical E + M, which nevertheless failed to explain "Anomalous" Zeeman Effect.

"Anomalous Zeeman effect"

More commonly, we see multiplets $\neq 3$!

$$-\frac{\hbar^2}{2m}\nabla^2\Psi = i\hbar\frac{\partial}{\partial t}\Psi \qquad \text{(free particle)}$$

This uses $E = \frac{p^2}{2m}$

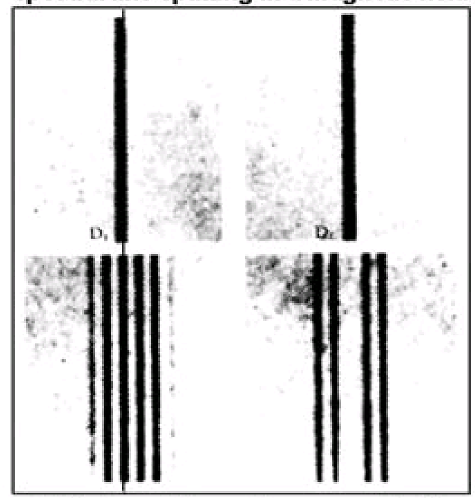
relativistic total energy

$$E = \sqrt{(mc^2)^2 + (pc)^2}$$

Note: $E = mc^2\sqrt{1 + \left(\frac{pc}{mc^2}\right)^2} \simeq mc^2\left(1 + \frac{1}{2}\left(\frac{pc}{mc^2}\right)^2 + \dots\right)$

$$= mc^2 + \frac{p^2}{2m} + \text{relativistic corrections}$$

The Zeeman effect
spectral line splitting in a magnetic field



note that each line splits symmetrically about its fundamental wavelength

Relativistic Quantum Mechanics

$$\sqrt{(mc^2)^2 + (pc)^2}\,\Psi = i\hbar \frac{\partial}{\partial t}\Psi \qquad \text{(free particle)}$$

Is LHS operator a perfect square?

$$m^2c^4 + p^2c^2 = \left(\alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j p_j c\right)^2$$

Only if: $\alpha_i^2 = 1$, $\alpha_i\alpha_j + \alpha_j\alpha_i = \{\alpha_i, \alpha_j\} = 0$, $i \neq j$

(This defines a "Clifford Algebra")

$$\left[\alpha_0 mc^2 + \sum_{j=1}^{3} \alpha_j p_j c\right]\Psi = i\hbar\frac{\partial}{\partial t}\Psi \qquad \text{"Dirac eqn"}$$

This puts space + time on same footing as required by relativity

"Irreducible representation" of "Clifford algebra"

4x4 matrices $\alpha_0 = \begin{bmatrix} \hat{I}_2 & \hat{0} \\ \hat{0} & -\hat{I}_2 \end{bmatrix}$, $\alpha_j = \begin{bmatrix} 0 & \sigma_j \\ \sigma_j & 0 \end{bmatrix}$, $j = 1, 2, 3$

"Pauli matrices": $\sigma_1 = \sigma_x = \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$, $\sigma_2 = \sigma_y = \begin{bmatrix} 0 & -i \\ i & 0 \end{bmatrix}$, $\sigma_3 = \sigma_z = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$

Dirac equation is then

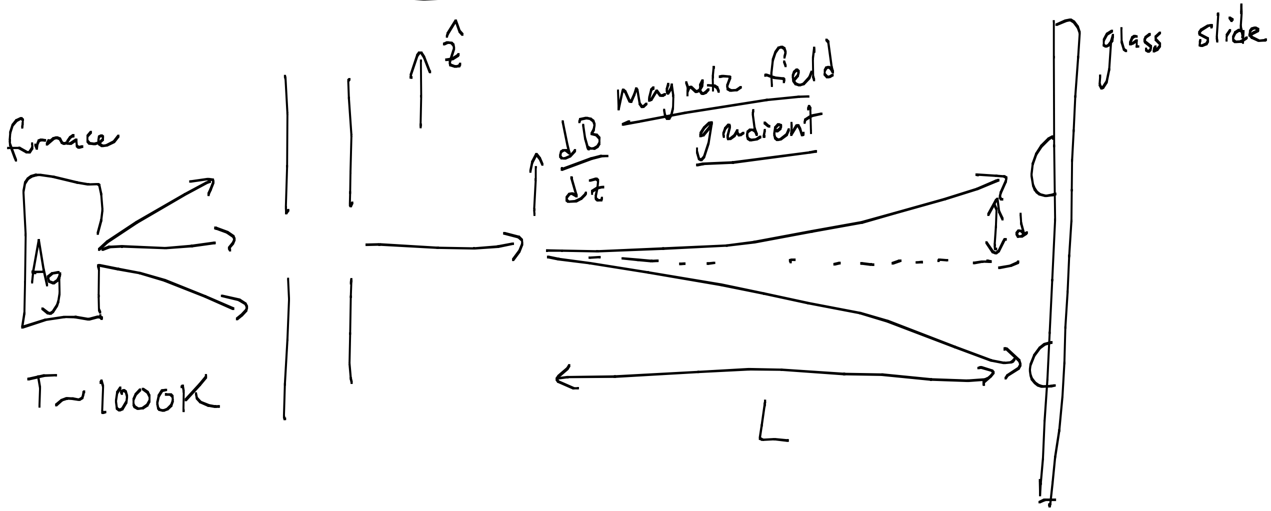
$$\begin{bmatrix} mc^2 \cdot \hat{I}_2 & (\vec{\sigma} \cdot \vec{p})c \\ (\vec{\sigma} \cdot \vec{p})c & -mc^2 \cdot \hat{I}_2 \end{bmatrix} \Psi = i\hbar \frac{\partial}{\partial t} \Psi$$

when $p = 0$, eigenvalues of relativistic Hamiltonian are $+mc^2$ and $-mc^2$

electrons ↗ positrons ↗

What do the two electron eigenvalues correspond to??

Stern - Gerlach experiment (1922)



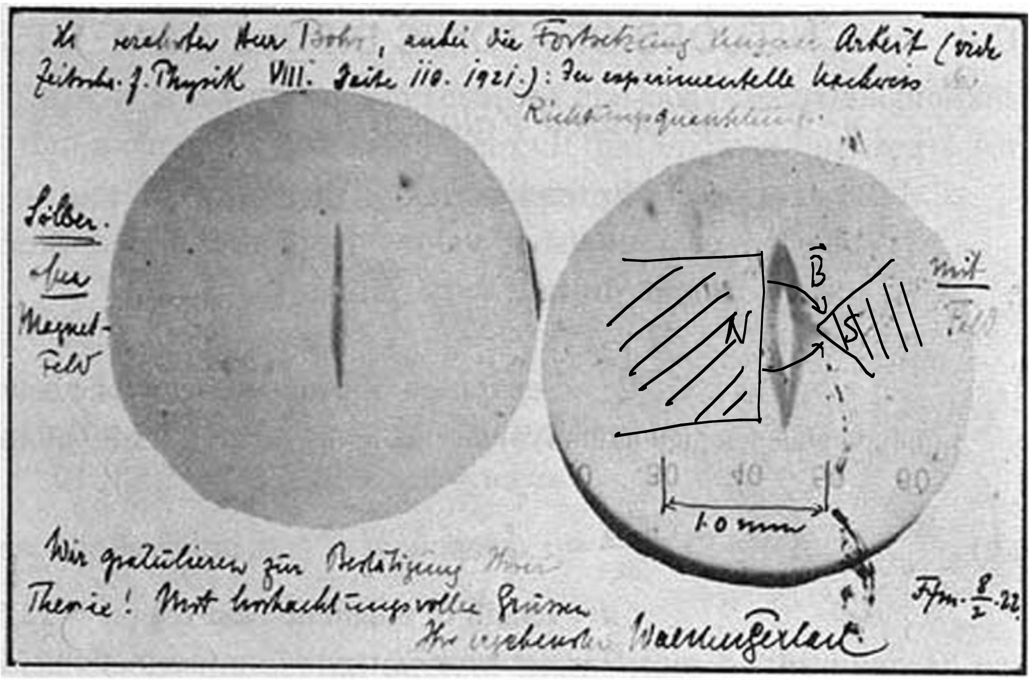
$$E = -\vec{\mu}\cdot\vec{B} \qquad F = -\frac{dE}{dz} = \vec{\mu}\cdot\frac{d\vec{B}}{dz} = \langle\mu_z\rangle\frac{dB}{dz}$$

$$d = \frac{1}{2}at^2 = \frac{1}{2}\frac{F}{m}\left(\frac{L}{v}\right)^2 = \frac{1}{2}\frac{\langle\mu_z\rangle\frac{dB}{dz}}{m}\frac{L^2}{v^2} = \frac{1}{6}\frac{\langle\mu_z\rangle\frac{dB}{dz}L^2}{\frac{1}{3}mv^2}$$

$$= \frac{1}{6}\frac{\langle\mu_z\rangle\frac{dB}{dz}L^2}{k_BT} = \frac{1}{\cancel{6}}\frac{(\cancel{5}.8\times10^{-5}\,\frac{eV}{T})(10\,\frac{T}{cm})(3.5\,cm)^2}{10^{-1}\,eV}$$

$$= 10^{-2}\,cm = 100\,\mu m$$

Experimental Results



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." (Physics Today December 2003)

Since this was done before true QM, S+G didn't know that the total orbital angular momentum of electrons in Ag is ZERO! The twofold splitting is therefore due to magnetic moment associated with intrinsic electron angular momentum, for which there is NO classical analogue! For historical reasons this is called "spin", $\vec{S}$.

So, $\langle \mu_z \rangle = \mu_B \frac{\langle S_z \rangle}{\hbar}$, $S_z = +\frac{\hbar}{2}, -\frac{\hbar}{2} = \hbar m_s$ and $m_s = +\frac{1}{2}, -\frac{1}{2}$. These correspond to the two components in the Dirac wavefunction! By convention, these states are often called "spin up" and "spin down" — the vector components are the amplitudes of these two states!