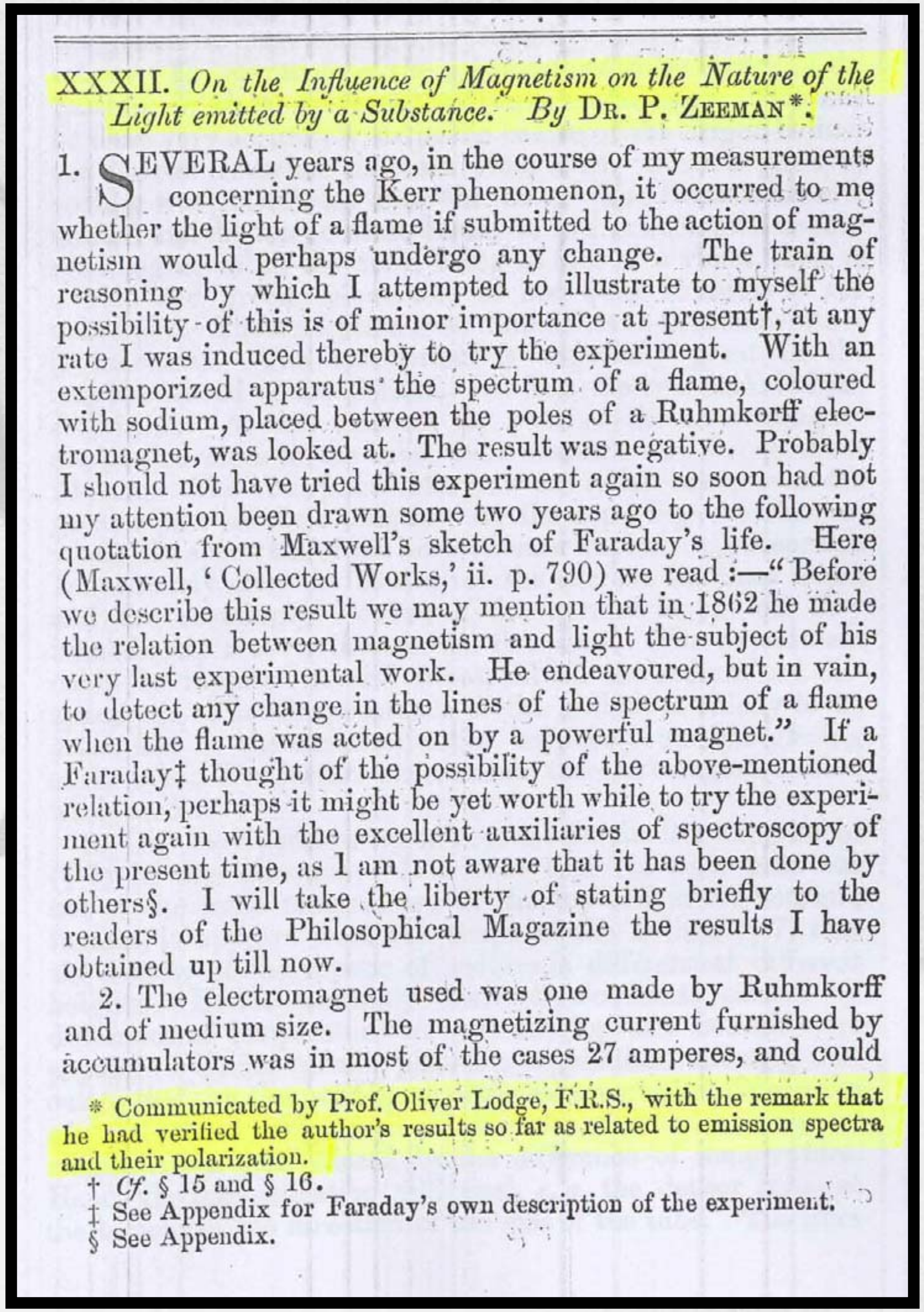
The anomalous Zeeman effect

P. Zeeman,
Philosophical Magazine **43**, 226 (1897)



XXXII. *On the Influence of Magnetism on the Nature of the Light emitted by a Substance.* By Dr. P. Zeeman*.

1. SEVERAL years ago, in the course of my measurements concerning the Kerr phenomenon, it occurred to me whether the light of a flame if submitted to the action of magnetism would perhaps undergo any change. The train of reasoning by which I attempted to illustrate to myself the possibility of this is of minor importance at present†, at any rate I was induced thereby to try the experiment. With an extemporized apparatus the spectrum of a flame, coloured with sodium, placed between the poles of a Ruhmkorff electromagnet, was looked at. The result was negative. Probably I should not have tried this experiment again so soon had not my attention been drawn some two years ago to the following quotation from Maxwell's sketch of Faraday's life. Here (Maxwell, 'Collected Works,' ii. p. 790) we read :—"Before we describe this result we may mention that in 1862 he made the relation between magnetism and light the subject of his very last experimental work. He endeavoured, but in vain, to detect any change in the lines of the spectrum of a flame when the flame was acted on by a powerful magnet." If a Faraday‡ thought of the possibility of the above-mentioned relation, perhaps it might be yet worth while to try the experiment again with the excellent auxiliaries of spectroscopy of the present time, as I am not aware that it has been done by others§. I will take the liberty of stating briefly to the readers of the Philosophical Magazine the results I have obtained up till now.

2. The electromagnet used was one made by Ruhmkorff and of medium size. The magnetizing current furnished by accumulators was in most of the cases 27 amperes, and could

* Communicated by Prof. Oliver Lodge, F.R.S., with the remark that he had verified the author's results so far as related to emission spectra and their polarization.

† *Cf.* § 15 and § 16.

‡ See Appendix for Faraday's own description of the experiment.

§ See Appendix.

Zeeman‘s experimental set-up and findings

3. Between the paraboloidal poles of an electromagnet, the middle part of the flame from a Bunsen burner was placed. A piece of asbestos impregnated with common salt was put in the flame in such a manner that the two D-lines were seen as narrow and sharply defined lines on the dark ground. The distance between the poles was about 7 mm. If the current was put on, the two D-lines were distinctly widened. If the current was cut off they returned to their original position. The appearing and disappearing of the widening was simultaneous with the putting on and off of the current. The experiment could be repeated an indefinite number of times.

4. The flame of the Bunsen was next interchanged with a flame of coal-gas fed with oxygen. In the same manner as in § 3, asbestos soaked with common salt was introduced into the flame. It ascended vertically between the poles. If the current was put on again the D-lines were widened, becoming perhaps three or four times their former width.

5. With the red lines of lithium, used as carbonate, wholly analogous phenomena were observed.

6. Possibly the observed phenomenon (§§ 3, 4, 5) will be regarded as nothing of any consequence. One may reason in

Zeeman‘s conclusions

11. The different experiments from §§ 3 to 9 make it more and more probable that the absorption- and hence also the emission lines of an incandescent vapour are widened by the action of magnetism. Now if this is really the case, then

… and yet another discovery:

Of course Zeeman could not give any coherent microscopic explanation of the phenomena he had discovered since not even Bohr's atomic model was around at his time. But, following an advice of Lorentz, he did discover another peculiar feature of his results, namely that the polarization state of the emitted light was also changed in the presence of an external magnetic field. "*The plate and the nicol were placed relatively in such a manner that right-handed circularly light was quenched. Now ... the widened line must at one edge be right handed circularly-polarized, at the other edge left-handed. By a rotation of the analyzer over 90° the light that was first extinguished will be transmitted and vice versa. .... This experiment could be repeated any number of times*".

Zeeman's discoveries offered quite a few hints for later theories, however, for these to get formulated not only the electronic spin had to be discovered [1], but also Schrödinger's wave mechanics [2] had to become relativistic [3] – [4].

1. G. E. Uhlenbeck and S. A. Goudsmit, Naturwiss. 13, 953 (1925), Nature 117, 264 (1926).
2. E. Schrödinger, Ann. Physik 81, 109 (1926).
3. W. Pauli, Z. Physik 43, 601 (1927).
4. P. A. M. Dirac, Proc. Roy. Soc. (London) A117, 610 (1928), A118, 351 (1928).

The Dirac operator for a central field

Let $\mathcal{H}_0$ be the (time-independent) Dirac Hamiltonian for a central field $V(|\vec{r}|)$

$$\mathcal{H}_0 = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V(|\vec{r}|)I_4 \quad , \tag{1}$$

corresponding to the boundary conditions of an atom

$$\lim_{r\to 0} r^2 V(|\vec{r}|) = 0 \quad , \quad \lim_{r\to\infty} V(|\vec{r}|) = 0 \quad , \tag{2}$$

where I_n denotes an n-dimensional unit matrix. In Eq. (1) $\vec{\alpha}$ and β refer to Dirac matrices,

$$\vec{\alpha} = \begin{pmatrix} 0 & \vec{\sigma} \\ \vec{\sigma} & 0 \end{pmatrix} \quad , \quad \beta = \begin{pmatrix} I_2 & 0 \\ 0 & -I_2 \end{pmatrix} \quad , \tag{3}$$

$\vec{\sigma}$ being a formal vector consisting of the Pauli spin matrices σ_x, σ_y, and σ_z,

$$\vec{\sigma} = (\sigma_x, \sigma_y, \sigma_z) \quad , \tag{4}$$

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad , \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \quad , \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad . \tag{5}$$

Wavefunctions & constants of motions

Because of the block-diagonal structure of β the wave functions $\psi^0(\vec{r})$ belonging to $\mathcal{H}_0$ are so-called bispinors,

$$\psi^0(\vec{r}) = \begin{pmatrix} \phi^0(\vec{r}) \\ \chi^0(\vec{r}) \end{pmatrix} \quad . \tag{6}$$

For a central field $\mathcal{H}_0$ has the following constants of motion

$$\left[\mathcal{H}_0, J^2\right]_- = [\mathcal{H}_0, J_z]_- = [\mathcal{H}_0, K]_- = 0 \quad , \quad K = \beta\left(\vec{\sigma}\cdot\vec{L} + 1\right) \quad , \tag{7}$$

that correspond to the well-known quantum numbers j, μ and κ in terms of the below eigenvalue equations

$$\begin{array}{cc} J^2\phi^0(\vec{r}) = j(j+1)\phi^0(\vec{r}) \quad , & J^2\chi^0(\vec{r}) = j(j+1)\chi^0(\vec{r}) \quad , \\ J_z\phi^0(\vec{r}) = \mu\phi^0(\vec{r}) \quad , & J_z\chi^0(\vec{r}) = \mu\chi^0(\vec{r}) \quad , \\ \left(\vec{\sigma}\cdot\vec{L} + 1\right)\phi^0(\vec{r}) = -\kappa\phi^0(\vec{r}) \quad , & \left(\vec{\sigma}\cdot\vec{L} + 1\right)\chi^0(\vec{r}) = \kappa\chi^0(\vec{r}) \quad . \end{array} \tag{8}$$

An eigenfunction of $\mathcal{H}_0$, J^2, J_z and K can therefore be written as

$$\psi^0_{\kappa\mu}(\vec{r}) = \begin{pmatrix} g_\kappa(r)\chi_{\kappa\mu}(\hat{r}) \\ if_\kappa(r)\chi_{-\kappa\mu}(\hat{r}) \end{pmatrix} \quad , \tag{9}$$

and fulfils the property

$$\left\langle \psi^0_{\kappa\mu}(\vec{r}) \right| \mathcal{H}_0 \left| \psi^0_{\kappa'\mu'}(\vec{r}) \right\rangle = \int \psi^0_{\kappa\mu}(\vec{r})^* \mathcal{H}_0 \psi^0_{\kappa'\mu'}(\vec{r}) d\Omega = E^0_{\kappa\mu} \delta_{\kappa\kappa'} \delta_{\mu\mu'} \quad , \tag{10}$$

$E^0_{\kappa\mu}$ being the $\kappa\mu$-th (one electron) eigenvalue for which because of the orthonormality of the spin spherical harmonics the following condition applies

$$E^0_{\kappa\mu} = E^0_\kappa \quad , \quad \forall \mu \in \{-j, -j+1, \ldots, j-1, j\} \quad . \tag{11}$$

In Eq. (9) the radial functions $g_\kappa(r)$ and $f_\kappa(r)$ are usually termed "large" and "small radial component" and the $\chi_{\kappa\mu}(\hat{r})$ are so-called spin spherical harmonics,

$$\chi_{\kappa\mu}(\hat{r}) = \sum_{s=\pm 1/2} C(\ell, j, \frac{1}{2} | \mu - s, s) Y_{\ell,\mu-s}(\hat{r}) \Phi_s \quad , \tag{12}$$

the $C(\ell, j, \frac{1}{2}|\mu - s, s)$ being the famous Clebsch-Gordan coefficients, and where the $Y_{\ell,\mu-s}(\hat{r})$ are spherical harmonics, and the Φ_s refer to the spin basis functions

$$\Phi_{1/2} = \begin{pmatrix} 1 \\ 0 \end{pmatrix}, \Phi_{-1/2} = \begin{pmatrix} 0 \\ 1 \end{pmatrix} \quad . \tag{13}$$

The „anomalous“ Zeeman effect

Suppose now one considers the presence of a homogeneous magnetic field $\vec{H}$. In this case the corresponding Dirac Hamiltonian is given by [7]

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}_1 \quad , \tag{14}$$

$$\mathcal{H}_1 = e\,\vec{\alpha} \cdot \vec{A} = -\frac{e}{2}\vec{\alpha} \cdot \vec{r} \times \vec{H} \quad . \tag{15}$$

Choosing $\vec{H}$ to point along the z direction,

$$\vec{H} || z : \mathcal{H}_1 = -\frac{e}{2}\left|\vec{H}\right|(\alpha_x y - \alpha_y x) \quad , \tag{16}$$

it is easy to see that the only (remaining) constant of motion of $\mathcal{H}$ is J_z,

$$[\mathcal{H}, J_z]_- = 0 \quad , \quad [\mathcal{H}, K]_- \neq 0 \quad , \quad \left[\mathcal{H}, J^2\right]_- \neq 0 \quad . \tag{17}$$

The matrix elements of $\mathcal{H}_1$ in the basis of the eigenfunctions of $\mathcal{H}_0$, see Eqs. (9) and (10),

$$\left\langle \psi^0_{\kappa\mu}(\vec{r})\right| \mathcal{H}_1 \left|\psi^0_{\kappa\mu}(\vec{r})\right\rangle = -\frac{ie\left|\vec{H}\right|}{2} R_{\kappa\kappa'} A_{\kappa\kappa'} \quad , \tag{18}$$

The radial and the angular parts of the integrals

$$R_{\kappa\kappa'} = \int_0^\infty r^3 \left(g_\kappa(r) f_{\kappa'}(r) + g_{\kappa'}(r) f_\kappa(r) \right) dr \quad , \tag{19}$$

and an angular part, which can be evaluated analytically

$$A_{\kappa\kappa'} = \int \left(\chi_{\kappa\mu}(\hat{r}) \left[\vec{\sigma} \times \vec{r} \right] \chi_{-\kappa\mu}(\hat{r}) \right) d\hat{r} \quad , \tag{20}$$

$$A_{kk} = \frac{4i\ell\mu}{4\ell^2 - 1} \quad ; \quad k = \ell \quad ,$$

$$A_{-k,-k} = -\frac{4i\,(\ell+1)\,\mu}{(2\ell+1)(2\ell+3)} \quad ; \quad k = \ell + 1 \quad ,$$

$$A_{k,-k} = i\frac{\left[(\ell + 1/2)^2 - \mu^2\right]^{1/2}}{(2\ell+1)} \quad ; \quad k = \ell \quad ,$$

$$A_{-k,k} = i\frac{\left[(\ell + 3/2)^2 - \mu^2\right]^{1/2}}{(2\ell+3)} \quad ; \quad k = \ell + 1 \quad .$$

Expanding a solution $\Psi(\vec{r})$ of the below Dirac equation,

$$\mathcal{H}\Psi(\vec{r}) = E\Psi(\vec{r}) \quad , \tag{21}$$

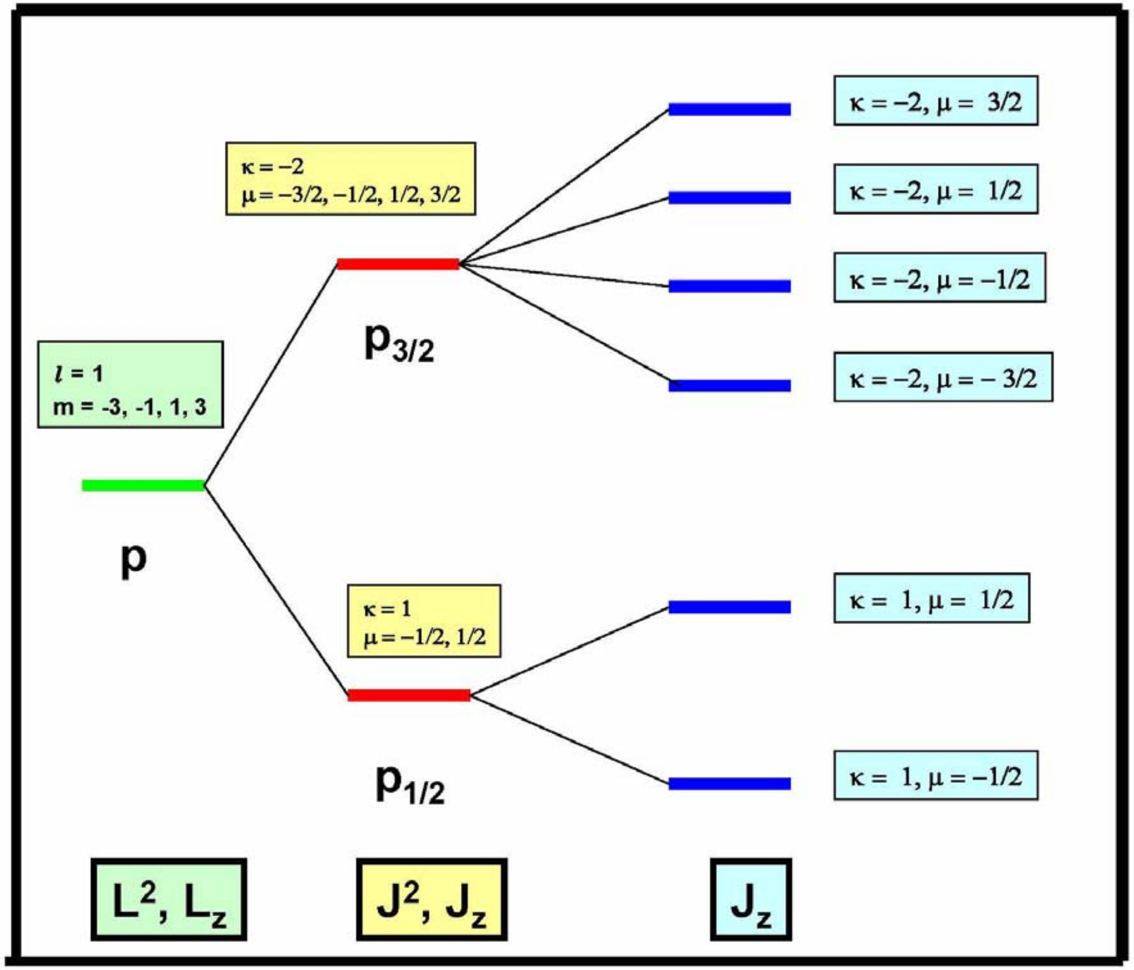
in the basis of the eigenfunctions of $\mathcal{H}_0$

$$\Psi(\vec{r}) = \sum_{\kappa,\mu} c_{\kappa\mu}\psi^0_{\kappa\mu}(\vec{r}) \quad , \tag{22}$$

one immediately gets the following set of equations

$$\begin{aligned}
\sum_{\kappa,\kappa'}\sum_{\mu,\mu'} c^*_{\kappa\mu}\left[\left\langle\psi^0_{\kappa\mu}(\vec{r})\right|\mathcal{H}\left|\psi^0_{\kappa'\mu'}(\vec{r})\right\rangle - E\delta_{\kappa\kappa'}\right]\delta_{\mu\mu'}c_{\kappa'\mu'} &= 0 \quad , \\
\sum_{\kappa\mu} c^*_{\kappa\mu}\sum_{\kappa'}\left[\left\langle\psi^0_{\kappa\mu}(\vec{r})\right|\mathcal{H}_1\left|\psi^0_{\kappa'\mu}(\vec{r})\right\rangle - \underbrace{(E-E^0_\kappa)}_{E'_{\kappa\mu}}\delta_{\kappa\kappa'}\right]c_{\kappa'\mu} &= 0 \quad , \qquad (23) \\
\sum_{\kappa,\kappa'}\sum_{\mu} c^*_{\kappa\mu}\left[-\frac{ie\left|\vec{H}\right|}{2}R_{\kappa\kappa'}A_{\kappa\kappa'} - E'_{\kappa\mu}\delta_{\kappa\kappa'}\right]c_{\kappa'\mu} &= 0 \quad . \qquad (24)
\end{aligned}$$

Schematic view of the Zeeman splitting:



Back to Zeeman‘s experiments:

the problem of emission spectroscopy. Assuming that – as usual – one can use an electric dipole approximation the transition probability per unit time is given by

$$P_{fi} = A_0^2 \left(\frac{E_f - E_i}{\hbar} \right)^2 |\langle\, f \mid \vec{u} \cdot \vec{p} \mid i \,\rangle|^2 \, \delta(E_f - E_i + \hbar\omega) \quad , \tag{25}$$

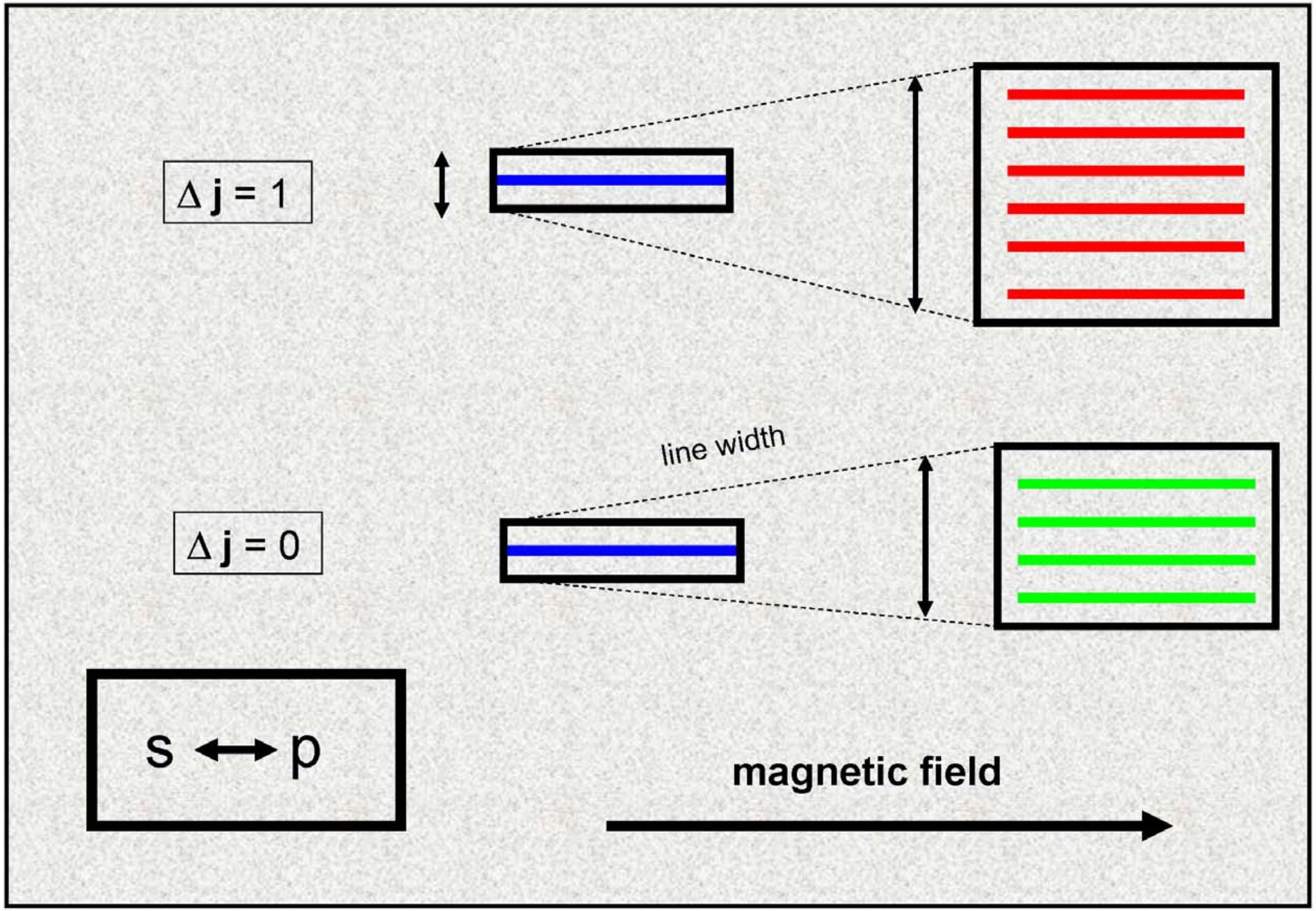
where i and f denote the initial and the final state, respectively, A_0 is the (properly normalized) amplitude of the vector potential and $\vec{u}$ the (classical) polarization vector, which stands perpendicular to the propagation direction of light. Considering now for matters of simplicity only the Dirac delta-function in Eq. (25), the so-called energy conservation condition, from Fig. (1) one can see that in the presence of a magnetic field even for a $\Delta j = 0$ transition four lines have to be observed experimentally. In general for a p to s transition the below situation applies,

	$\Delta j = 0$	$\Delta j = 1$
non relativistic		$s \leftarrow p$
relativistic $\lvert\vec{H}\rvert = 0$	$s_{1/2} \leftarrow p_{1/2}$	$s_{1/2} \leftarrow p_{3/2}$
relativistic $\lvert\vec{H}\rvert \neq 0$	$s_{1/2}^{1/2} \leftarrow p_{1/2}^{1/2},\ p_{1/2}^{-1/2}$	$s_{1/2}^{1/2} \leftarrow p_{3/2}^{1/2},\ p_{3/2}^{-1/2},\ p_{3/2}^{3/2}$
	$s_{1/2}^{-1/2} \leftarrow p_{1/2}^{-1/2},\ p_{1/2}^{1/2}$	$s_{1/2}^{-1/2} \leftarrow p_{3/2}^{-1/2},\ p_{3/2}^{1/2},\ p_{3/2}^{-3/2}$

which clearly shows how confusing the so-called Zeeman splitting must have been for many years [8].

Polarization state of the emitted light

This now was Zeeman's famous experiment:



5 The importance of the Zeeman effect

In order to appreciate the importance of Zeeman's findings in modern physics one might consider an effective one-electron Dirac Hamiltonian for a magnetic system such as given by Density Functional theory [9]

$$\mathcal{H} = c\vec{\alpha} \cdot \vec{p} + \beta mc^2 + V(\vec{r}) I_4 + \beta \vec{\Sigma} \cdot \vec{B}(\vec{r}) \quad , \tag{26}$$

where $V(\vec{r})$ is the effective potential and $\vec{B}(\vec{r})$ the effective exchange (magnetic) field,

$$V(\vec{r}) = V^{eff}[n, \vec{m}] = V^{ext} + V^H + \frac{\delta E_{xc}[n, \vec{m}]}{\delta n} \quad , \tag{27}$$

$$\vec{B}(\vec{r}) = \vec{B}^{eff}[n, \vec{m}] = \vec{B}^{ext} + \frac{e\hbar}{2mc} \frac{\delta E_{xc}[n, \vec{m}]}{\delta \vec{m}} \quad , \tag{28}$$

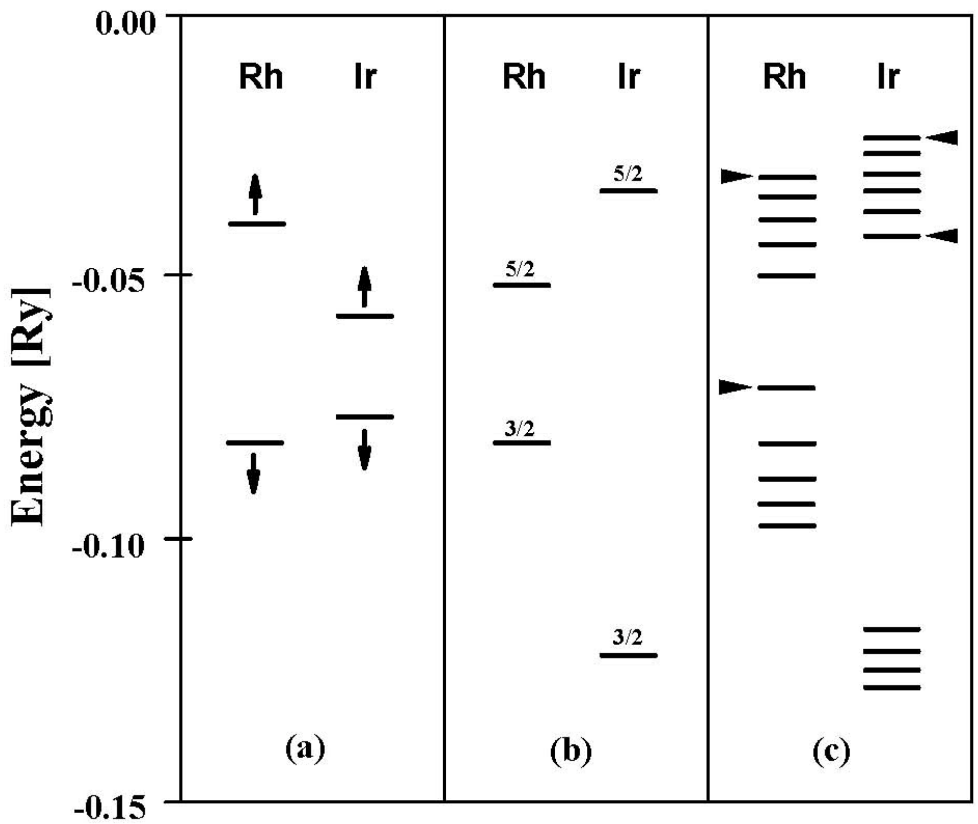
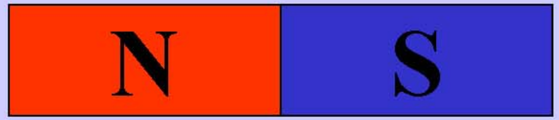


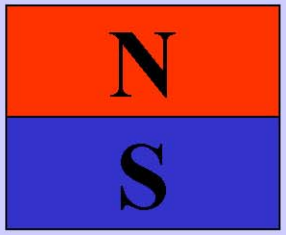
Figure 3: Calculated positions of d-like resonances of a Rh and an Ir overlayer on Ag(100). Panel (a) refers to the non-relativistic spin-polarized case, where the spin-up and spin-down channels are denoted by up and down arrows. The relativistic non-magnetic case is shown in panel (b) illustrating the spin-orbit splitting between the $j = 3/2$ and $j = 5/2$ resonances. The relativistic spin-polarized case, see Eq. (26), is displayed in panel (c). The uncoupled resonances corresponding to $(j, \mu) = (5/2, -5/2)$ (upper ones) and $(5/2, 5/2)$ lower ones are indicated by small horizontal arrows. From [11].

Optical Devices:

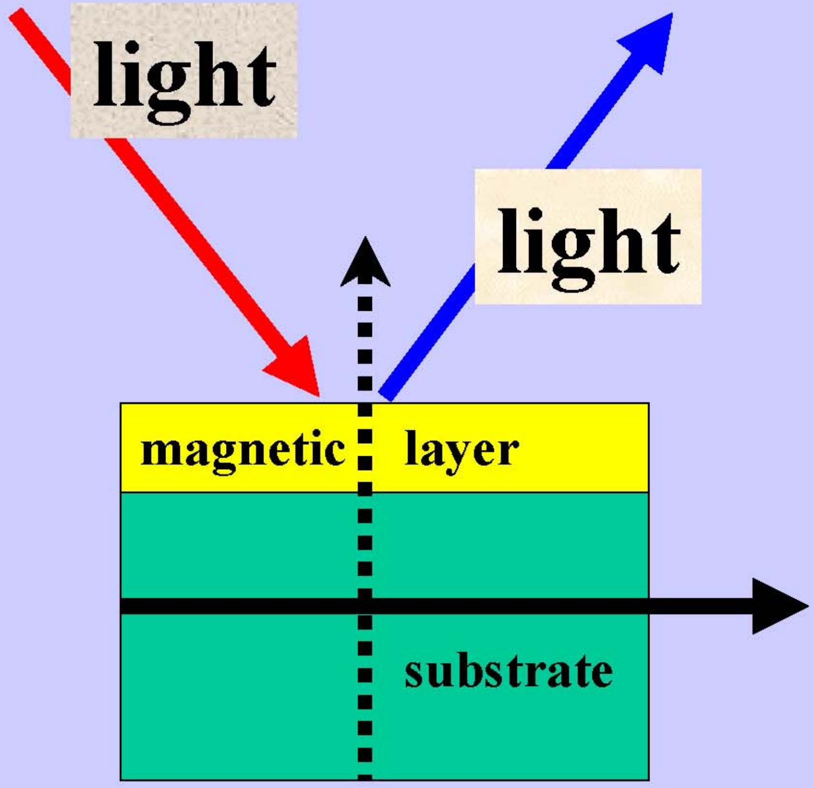
Magnetization



in-plane

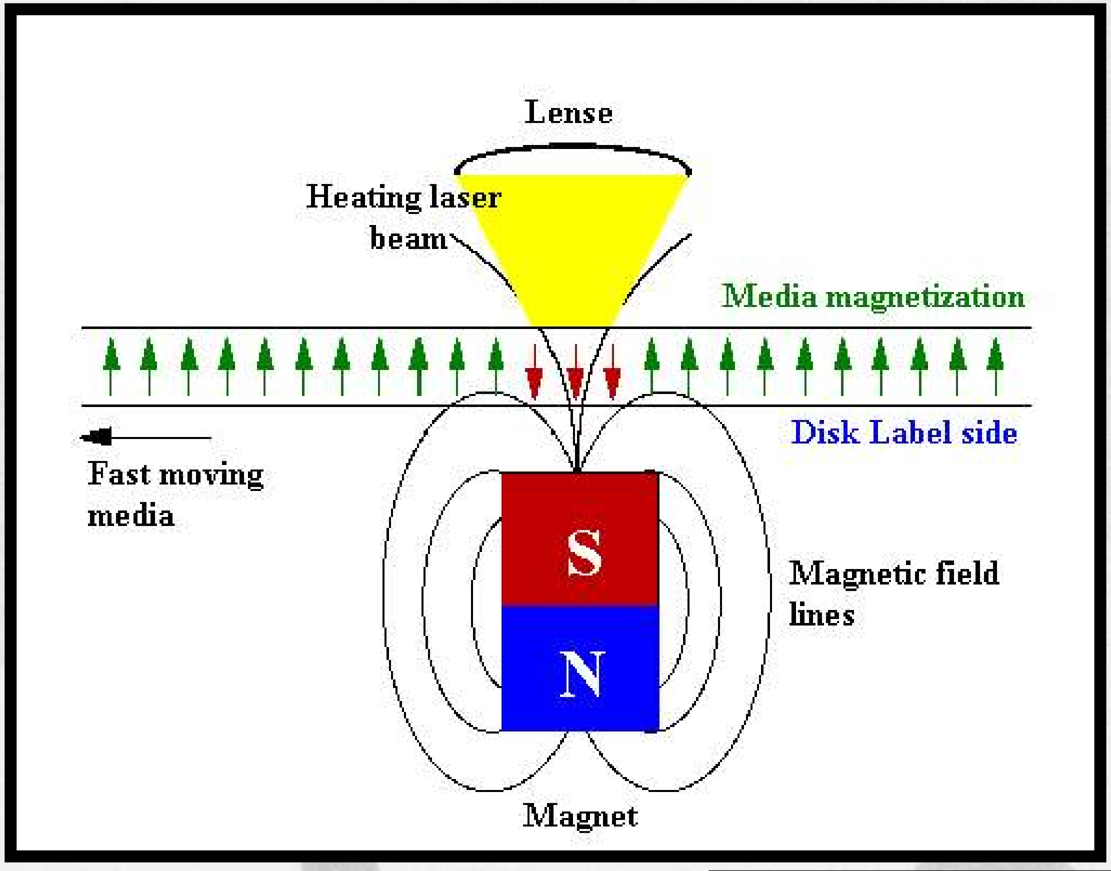


perpendicular



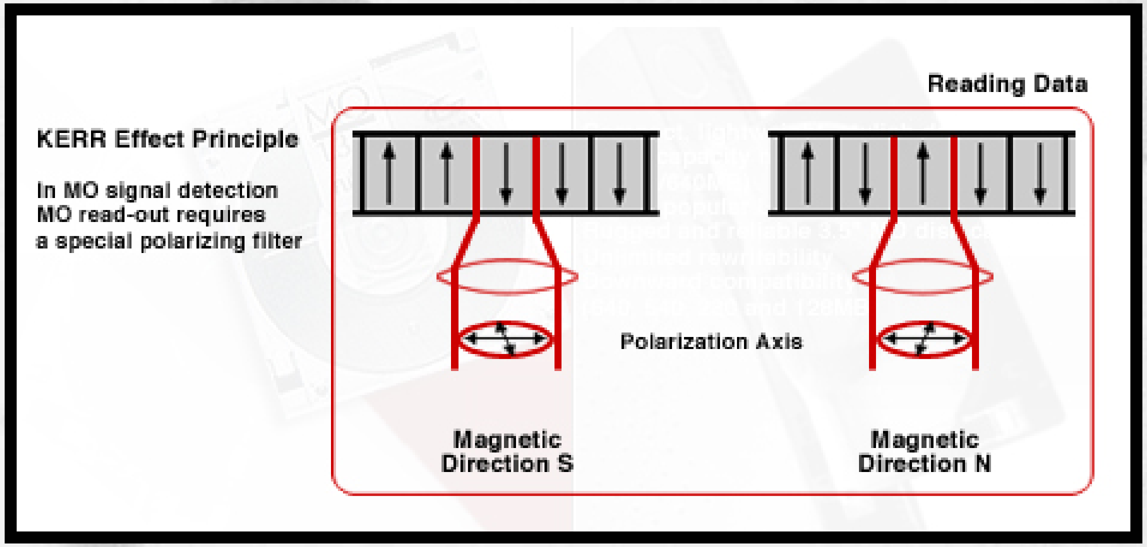
MO Kerr effect

Magneto-optical discs



Write

Read



Our own conclusions: the phenomenon that was observed by Zeeman turned out to be of crucial importance!!!

3. Between the paraboloidal poles of an electromagnet, the middle part of the flame from a Bunsen burner was placed. A piece of asbestos impregnated with common salt was put in the flame in such a manner that the two D-lines were seen as narrow and sharply defined lines on the dark ground. The distance between the poles was about 7 mm. If the current was put on, the two D-lines were distinctly widened. If the current was cut off they returned to their original position. The appearing and disappearing of the widening was simultaneous with the putting on and off of the current. The experiment could be repeated an indefinite number of times.

4. The flame of the Bunsen was next interchanged with a flame of coal-gas fed with oxygen. In the same manner as in § 3, asbestos soaked with common salt was introduced into the flame. It ascended vertically between the poles. If the current was put on again the D-lines were widened, becoming perhaps three or four times their former width.

5. With the red lines of lithium, used as carbonate, wholly analogous phenomena were observed.

6. Possibly the observed phenomenon (§§ 3, 4, 5) will be regarded as nothing of any consequence. One may reason in