Complex Atoms

4 Quantum numbers

Several quantum numbers: n, l, m_l, s, m_s

Lifting the l -degeneracy

Magnetic effects

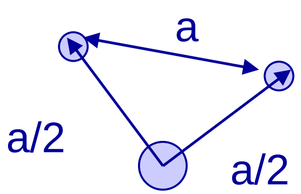
Spin

Otto Stern

Pieter Zeeman

Hendrik Lorentz

The Helium atom; semi-classical approximation



Without repulsion:

$$E = 2E_1 = -2Z^2 E_0 = -8\cdot(13.6)eV = -108.8eV$$

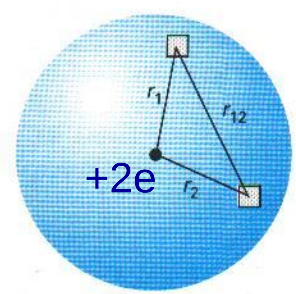
With repulsion; electrons at fixed distance ~a_0,
Repulsive energy:

$$\frac{e^2}{4\pi\varepsilon_0 a_0} = \alpha\hbar c \frac{\alpha m_e c}{\hbar} = 2E_0 = 27.2eV$$

Calculated: $E_{tot} = -81.6eV$

Experimental: $E_{tot} = -79eV$

Complex Atoms and the Schrödinger Equation



$$H = -\frac{\hbar^2}{2m_e}\left(\nabla_1^2 + \nabla_2^2\right) - \frac{2e^2}{4\pi\varepsilon_0 r_1} - \frac{2e^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}$$

E_{kin} attraction repulsion

NB: A non-central force

Two-particle Schrödinger equation: $H\Psi(\vec{r}_1,\vec{r}_2) = E\Psi(\vec{r}_1,\vec{r}_2)$

First approximation: unperturbed system (no repulsion) $H^{(0)} = H_1 + H_2$

Each: $H_i = -\frac{\hbar^2}{2m_e}\nabla_i^2 - \frac{2e^2}{4\pi\varepsilon_0 r_i}$ has solution $E_i = -R\frac{Z^2}{n_1^2} = -R\frac{4}{n_1^2}$

Wave function: $\Psi(\vec{r}_1,\vec{r}_2) = \psi_{nlm}(\vec{r}_1)\psi_{nlm}(\vec{r}_2) = \psi_1\psi_2$

$$H^{(0)}\Psi(\vec{r}_1,\vec{r}_2) = (H_1 + H_2)\psi_1\psi_2 = (H_1\psi_1)\psi_2 + \psi_1(H_2\psi_2)$$

$$= E_1\psi_1\psi_2 + E_2\psi_1\psi_2 = E\psi_1\psi_2$$

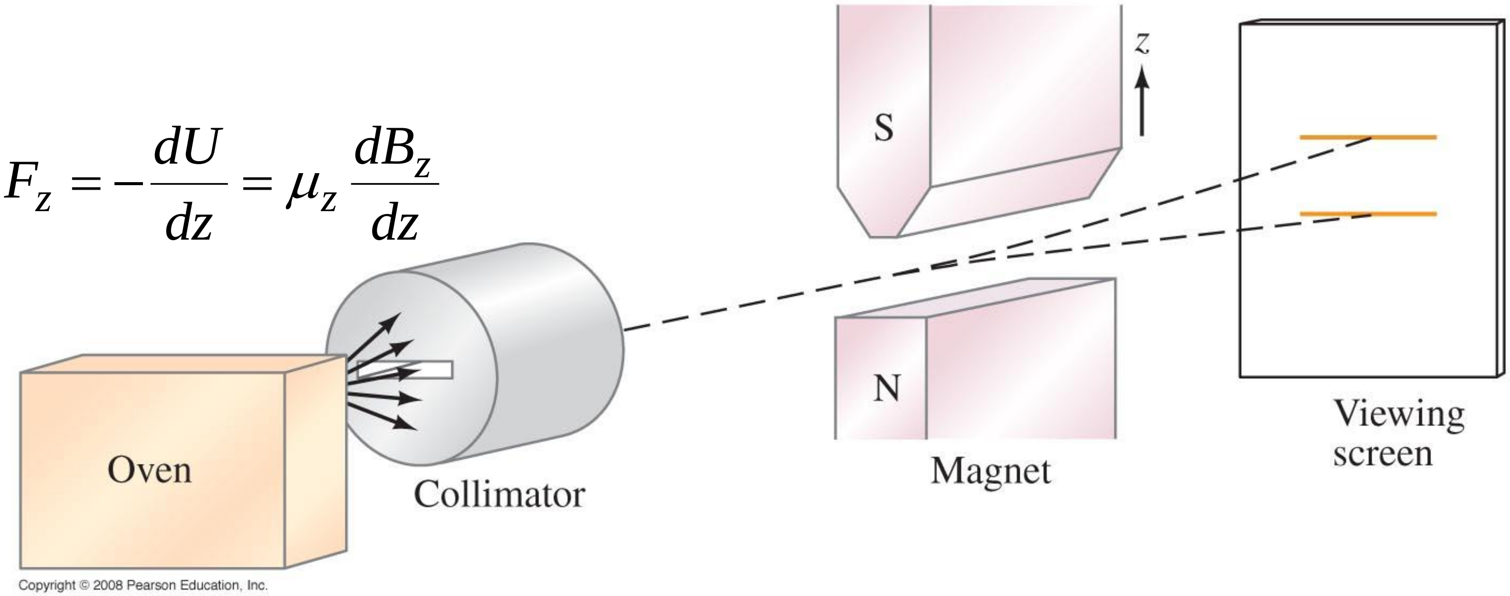
Hence: $$E = -4R\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

General rule: complex atoms → Product wave functions of hydrogen orbitals

Magnetic Dipole Moments; Space quantization

Stern-Gerlach experiment
-nonuniform magnetic field
-classically a continuum of deflection angles is expected
Instead, the angles were quantized, corresponding to the quantized values of the magnetic moment.

$$F_z = -\frac{dU}{dz} = \mu_z \frac{dB_z}{dz}$$



General for a magnetic dipole:
-Force on a dipole in a gradient
-Orientation of a dipole in a Homogeneous B-field


Otto Stern
The Nobel Prize in Physics 1943
"for his contribution to the development of the molecular ray method and his discovery of the magnetic moment of the proton"

Magnetic Dipoles

Potential Energy of a magnetic dipole $$U = -\vec{\mu} \cdot \vec{B}$$

Choose the magnetic field along z; $$U = -\mu_z B_z$$

Force = gradient of the potential:

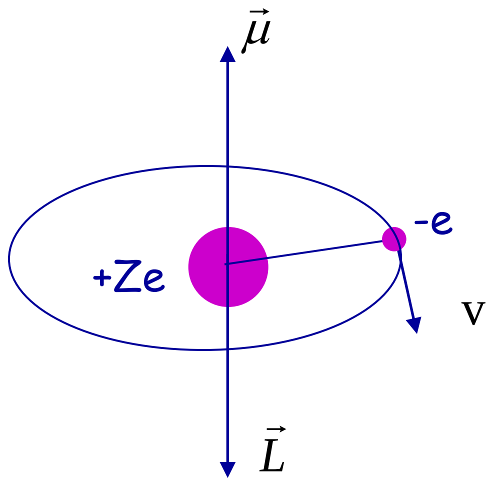
$$F_z = -\frac{dU}{dz} = \frac{d\mu_z B_z}{dz} = \mu_z \frac{dB_z}{dz}$$

1. Only a force if there is a magnetic field gradient ⟶ Stern-Gerlach space quantisation

2. In a homogeneous magnetic field ⟶ Zeeman effect

Both effects related to quantisation of angular momentum

Angular momentum and the unit of the Bohr magneton



Current (charge passing per time)

$$I = \frac{e}{T} = \frac{e\mathrm{v}}{2\pi r}$$

Magnetic moment

$$\mu = IA = \frac{e\mathrm{v}\pi r^2}{2\pi r}$$

Angular momentum

$$L = m_e \mathrm{v} r$$

Hence $\vec{\mu} = -\frac{e}{2m_e}\vec{L}$

Define $\mu_B = \frac{e\hbar}{2m_e}$ Bohr magneton

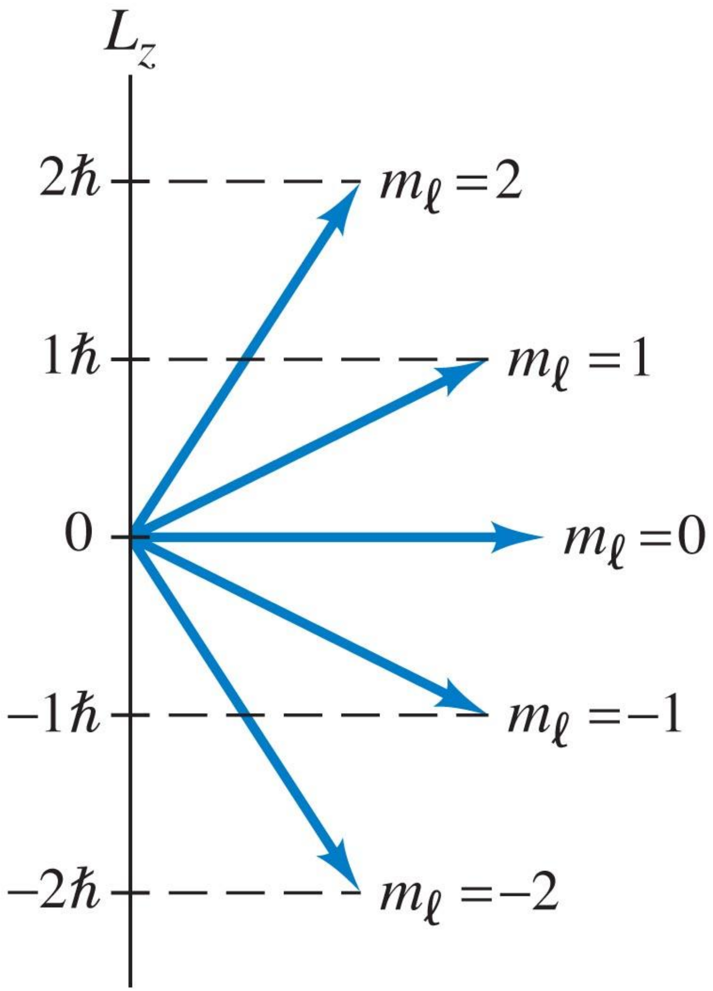
We find a relation between the angular momentum and the magnetic moment of a classical point charge

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

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

If no magnetic field: energy does not depend on m

m_l degeneracy



In a magnetic field

$$U = -\vec{\mu} \cdot \vec{B} = -\mu_z B_z$$

$$\mu_z = -\mu_B \frac{L_z}{\hbar}$$

For atomic wave functions;

$$L_z \Psi = m\hbar \Psi$$

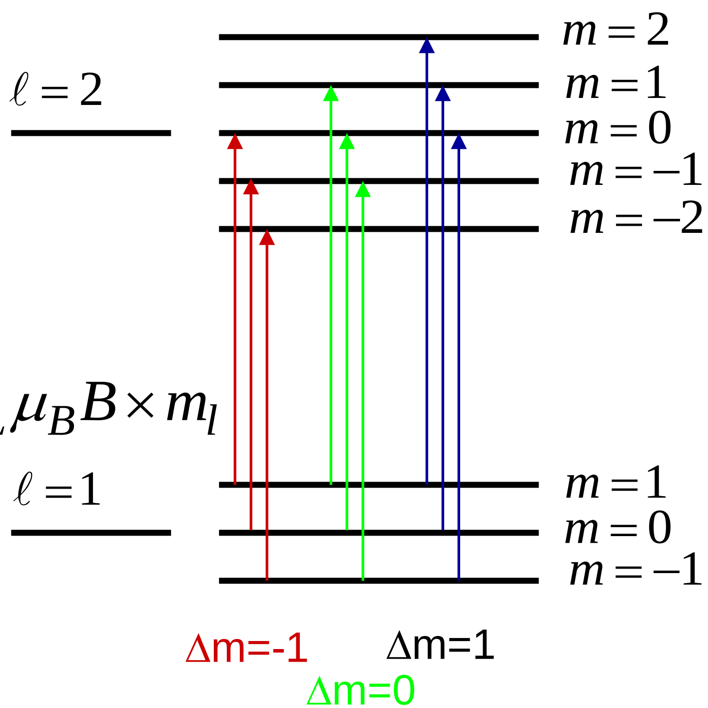
Hence splitting

$$U = \mu_B m_l B$$

Hydrogen Atom: The Zeeman effect

In a magnetic field, the energy levels split depending on m_ℓ.

For an $^1P \rightarrow {}^1D$-transition



$$U = g_L \mu_B B \times m_l$$

9 transitions
3 spectral lines (in hydrogen)

Pieter Zeeman

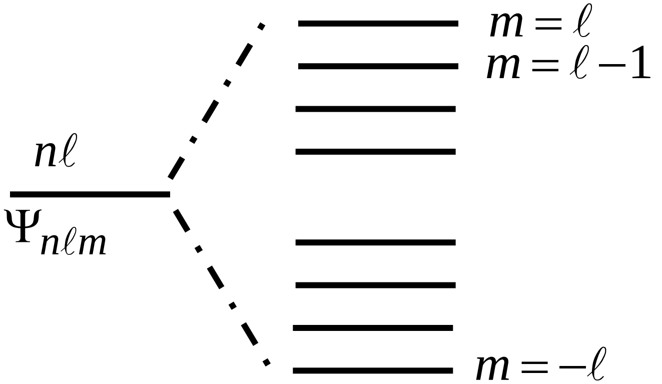
1902

Hendrik Lorentz

"in recognition of the extraordinary service they rendered by their researches into the influence of magnetism upon radiation phenomena"

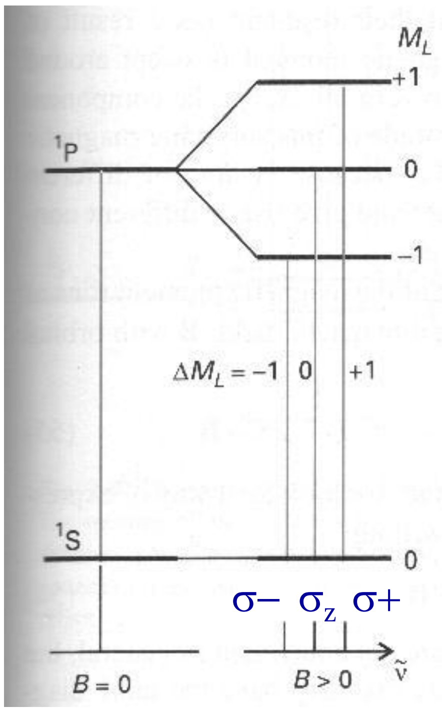
Normal Zeeman effect

Energy splitting for an *nl* state



Energy splitting: $\delta E_m = g\mu_B M$

For an ${}^1S \rightarrow {}^1P$-transition

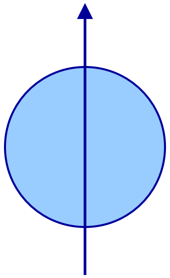


Recall selection rules for *m* and polarization of light

Electron spin

No classical analogue for this phenomenon

$$s = \frac{1}{2}\hbar$$

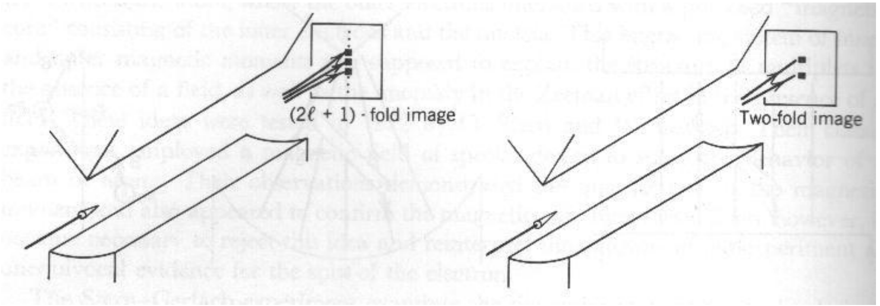


There is an additional “two-valuedness” in the spectra of atoms, behaving like an angular momentum

This may be interpreted/represented as an angular momentum

Origin of the spin-concept

-Stern-Gerlach experiment; space quantization



-Theory: the periodic system requires an **additional** two-valuedness

For a (relativistic) spin

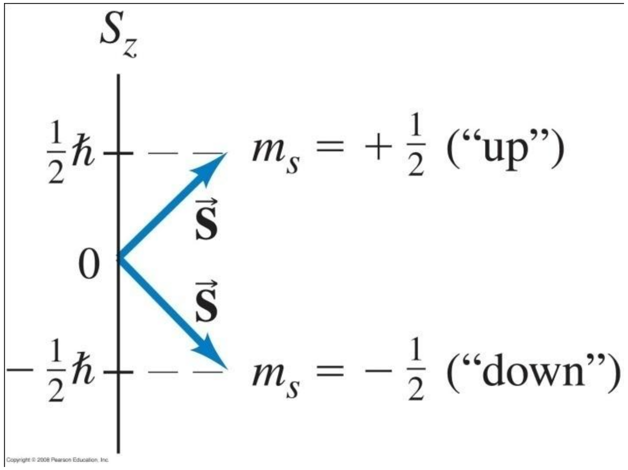
$$\vec{\mu}_S = -g_S \mu_B \frac{\vec{S}}{\hbar}$$

$$g_S = 2$$

This is peculiar !

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

The spin quantum number, m_s, for an electron can take on the values +½ and -½. The need for this quantum number was found by experiment; spin is an intrinsically quantum mechanical quantity, although it mathematically behaves as a form of angular momentum.



An additional quantum number !

Hydrogen Atom:
Schrödinger Equation and Quantum Numbers

TABLE 39–1 Quantum Numbers for an Electron

Name	Symbol	Possible Values
Principal	n	$1, 2, 3, \cdots, \infty$.
Orbital	ℓ	For a given n: ℓ can be $0, 1, 2, \cdots, n-1$.
Magnetic	m_ℓ	For given n and ℓ: m_ℓ can be $\ell, \ell-1, \cdots, 0, \cdots, -\ell$.
Spin	m_s	For each set of n, ℓ, and m_ℓ: m_s can be $+\frac{1}{2}$ or $-\frac{1}{2}$.