Atoms

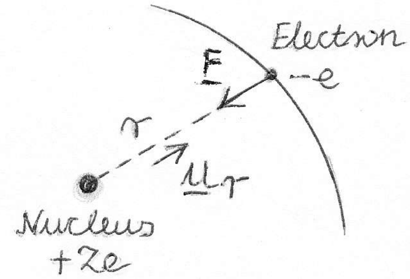
size $\sim 10^{-10}$ m (nucleus $\sim 10^{-14}$ m)

- nucleus A (mass number) particles, of these
  Z (atomic number) protons
  $N = A - Z$ neutrons } nucleons
  nuclear charge: $+Ze$
- Z electrons with charge $-e$ } Electromagnetic interaction

- $m_{nucleon} \simeq 1850\, m_{electron}$

Atomic properties (eletromagnetic, elastic, etc.) are determined by the electrons

The Hydrogen atom



$A = 1$, $Z = 1$

Assume: nucleus stationary
point like, charge Ze

Coulomb force: $\underline{F} = -\dfrac{Ze^2}{4\pi\varepsilon_0 r^2}\underline{u}_r$

The potential energy: $E_p(r) = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$

Schrödinger equation:

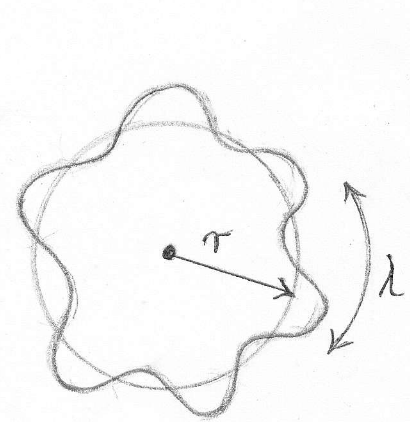
$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) - \frac{Ze^2}{4\pi\varepsilon_0 r}\psi = E\psi$$

Looking for stationary states and their energies

Semiclassical approach (Bohr)

Analogous with the potential box

Electron → standing wave on a circular orbit



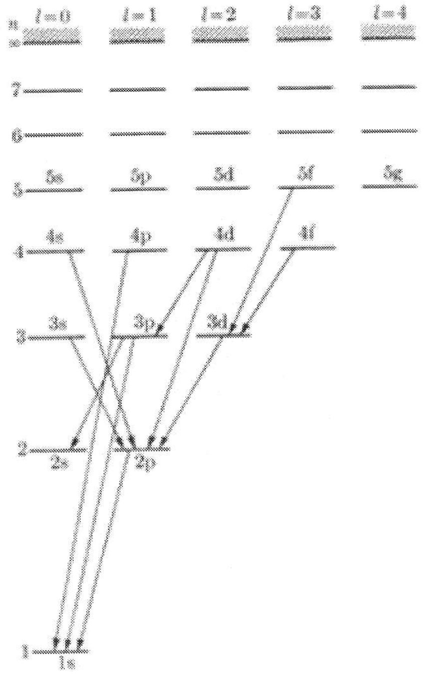
λ is the wavelength of the electron

$2\pi r = n\lambda$ for a standing wave

$r_n = \dfrac{n\lambda}{2\pi}$ $\quad L = r \cdot p = \dfrac{n\lambda}{2\pi}\dfrac{h}{\lambda} = n\hbar$ $\quad \left(p = \hbar k = \dfrac{h}{2\pi}\cdot\dfrac{2\pi}{\lambda} = \dfrac{h}{\lambda}\right)$

H atom: quantum mechanical analysis

- State: characterized by multiple quantum numbers n, l, m_l
- For given n
  l is between $0 - (n-1)$
  $\rightarrow n$ states with different l-s
- ns, np, nd states ($l = 0, 1, 2$)
  with the same energy
  (for $F \propto \frac{1}{r^2}$ only)
- In other central potentials:
  energy depends on n and l
  but not on m_l (direction)



Selection rules $\Delta l = \pm 1$ Δm_l
because of conservation of angular momentum
Angular momentum of the photon $\equiv 1$
Metastable states (e.g. 2s) 2s → 1s transition is forbidden (dipole approx.)

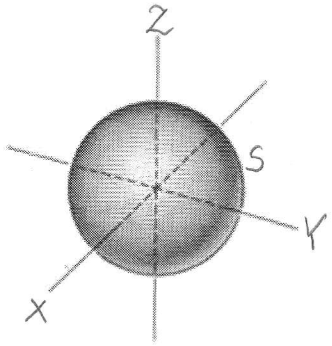
Orbit $\xrightarrow{q.m.}$ Wave function
Schrödinger equation in central force field
Shown earlier: $\psi(r, \theta, \varphi) = R(r) \cdot Y(\theta, \varphi)$
Due to the central symmetry $Y(\theta, \varphi)$ is identical for all central potential, determined by $|L|$ and L_z
$l, m_l \rightarrow Y_{l, m_l}(\theta, \varphi)$ spherical harmonic functions

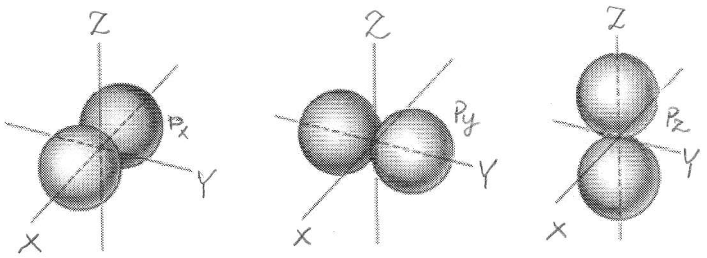
	l	m_l	Y_{l,m_l}
s	0	0	$Y_{00} = \frac{1}{\sqrt{4\pi}}$
p	1	0	$Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$
		± 1	$Y_{1\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\, e^{\pm i\varphi}$
d	2	0	$Y_{20} = \frac{1}{2}\sqrt{\frac{5}{4\pi}}(3\cos^2\theta - 1)$
		± 1	$Y_{2\pm1} = \mp\sqrt{\frac{15}{8\pi}}(\sin\theta\cos\theta)e^{\pm i\varphi}$
		± 2	$Y_{2\pm2} = \frac{1}{4}\sqrt{\frac{15}{2\pi}}(\sin^2\theta)e^{\pm i2\varphi}$

$$\psi_{n,l\,m_l}(r,\theta,\varphi) =$$
$$= R_{nl}(r)\, Y_{l\,m_l}(\theta,\varphi)$$

ψ is the superposition of such directional (Y) and R radial distibutions

l larger $\rightarrow$ more complicated



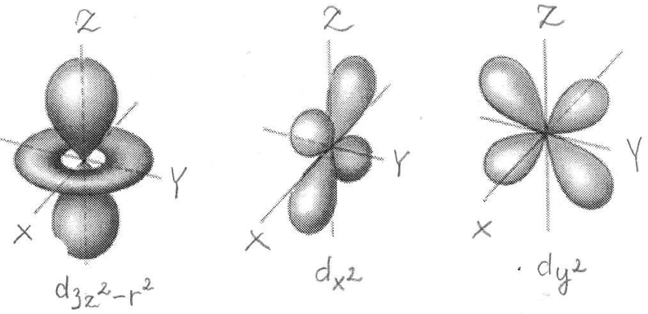


$|m_l| = 1$ $|m_l| = 1$ $|m_l| = 0$

p

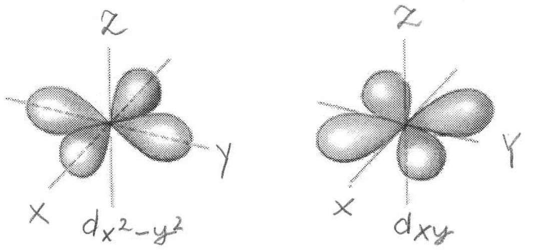
Real parts
Eigenfunctions of l, and $|m_l|$

$|m_l| = 0$



$|m_l| = 1$

d

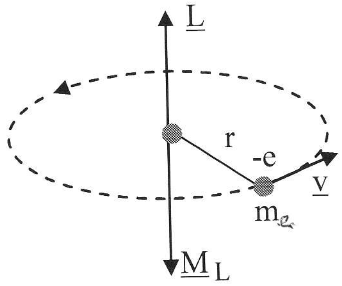


$|m_l| = 2$

Quantum mechanics/6.

Zeeman effect
spin
total angular moment

Experiment: atomic spectral lines split into triplets in strong magnetic field



Zeeman effect

Charged particle + angular momentum
circular current → magnetic dipole moment

$$\underline{L} = m_e \cdot \omega r^2$$

$$M_L = (\text{circ. current}) \cdot (\text{enclosed area}) = \frac{e}{T_{rot}} \cdot r^2 \pi$$

$$= \frac{e\omega}{2\pi} r^2 \pi = \frac{1}{2} e \omega r^2 = \frac{e}{2 m_e} L$$

Due to the negative electron charge:

$$\underline{M}_L = -\frac{e}{2 m_e} \underline{L}$$

z component of the magnetic moment

$$M_{L_z} = -\frac{e}{2 m_e} L_z = -\frac{e\hbar}{2 m_e} m_\ell = -\mu_B m_\ell$$

$$\mu_B = \text{Bohr magneton} = \frac{e\hbar}{2 m_e} = 9{,}3 \cdot 10^{-24}\, JT^{-1}$$

Atom in an external $\underline{B}$ magnetic field receives magnetic energy $E_B = -\underline{M} \cdot \underline{B} = \frac{e}{2 m_e} \underline{L} \cdot \underline{B}$

Let the z axes be ∥ with $\underline{B}$

$E_B = \mu_B \cdot B \cdot m_\ell$ where $B = |\underline{B}|$

But for an orbital with given $\ell \to 2\ell+1$ different m_ℓ's

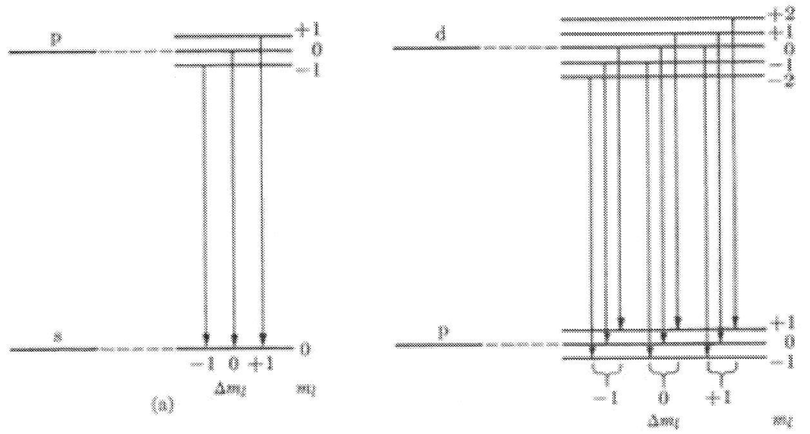
→ $2\ell+1$ different discreet E_B values

(corresponds to $2\ell+1$ different orientations of $\underline{L}$ relative to $\underline{B}$)

Energy of the electron

$E = E_n + E_B$

$\rightsquigarrow \forall\ (n, l)$ level splits into $(2l+1)$ levels with different energies



- p state : $l = 1$ $\quad m_l = +1, 0, -1$ $\quad$ 3 levels – triplet

p – s transition : triplet / 3 lines)

$m_l = 0 \longrightarrow m_l = 0$ $\quad$ with the original frequency

$m_l = \pm 1 \longrightarrow m_l = 0$ $\quad \nu + \Delta\nu$

$$\Delta \nu = \pm \frac{\mu_B \cdot B}{h} = 1{,}4 \cdot 10^{10} \cdot B \ [Hz]$$

- d state : $l = 2$ $\quad m_l = 0, \pm 1, \pm 2$ $\quad$ 5 levels

but selection rule : $\Delta m_l = 0, \pm 1$!

d – p transition 9 possibilitées, but when Δm_l is identical $\Delta \nu$ is the same

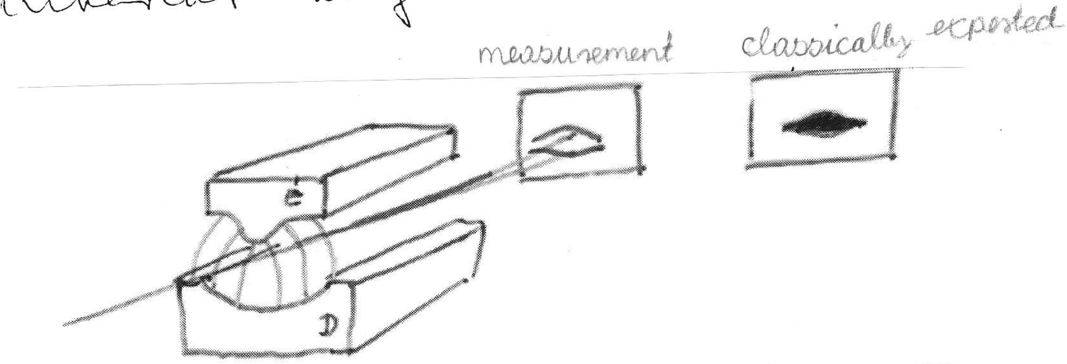
Δm_l can be $0, \pm 1$ only → triplet / 3 lines /

The Zeeman effect is the experimental proof of the quantization of the angular momentum.

/ If $\underline{L}$ were a continuous variable it could stand at arbitrary direction relative to $\underline{B}$ instead of splitting → broadening would be observed in an external magnetic field /

Electron spin

Stern - Gerlach experiment:
In an inhomogenous magnetic field H- like atoms (with s electron ground states : $l = 0$) for which $\underline{M}_L = 0$, deviate ⤳ They posess an inherent magnetic moment ; $\underline{M}_S$



$|\underline{B}|$ increases toward the north pole $\quad \underline{F} = \text{grad}(\underline{M} \cdot \underline{B})$

Magnetic dipole : if $\underline{M} \uparrow\uparrow \underline{B}$ → shifted toward increasing $|\underline{B}|$
if $\underline{M} \uparrow\downarrow \underline{B}$ → " " decreasing $|\underline{B}|$

Measurement → 2 kinds of dipole moments ⤳
The inherent magnetic moment of the electrons is also quantized $\underline{M}_s$

$\underline{M}_s$ is associated with angular momentum $\underline{S}$ ≡ spin

spin : 2 states $\quad (2s+1) = 2 \quad ⤳ s = \frac{1}{2}$

$$\underline{M}_S = - g_s \frac{e}{2m_e} \underline{S} \qquad g_s = \text{gyromagnetic factor} = 2$$

The total magnetic moment

$$\underline{M} = \underline{M}_L + \underline{M}_S = - \frac{e}{2m_e} (\underline{L} + g_s \cdot \underline{S})$$

The 2 states of electronspin are parallel or antiparallel with the magnetic field

For the angular momentum

l given $\rightarrow$ $2l+1$ different directions

For the spin

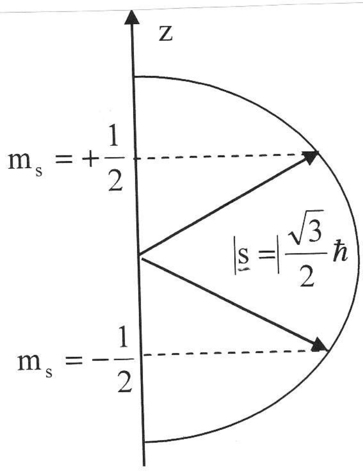
2 directions $\leadsto$ $l = \frac{1}{2}$

quantum numbers: $s, m_s \rightarrow s = \frac{1}{2}$ $m_s = \pm \frac{1}{2}$

Spin $\rightarrow$ physical quantity $\leadsto$ operator $\hat{\underline{S}}$

$S^2 = s(s+1)\hbar^2 = \frac{3}{4}\hbar^2$ $s = \frac{1}{2}$

$S_z = m_s \hbar$ $m_s = \pm \frac{1}{2}$



Spin wavefunctions:

χ_{m_s}

$\hat{S}^2 \cdot \chi_{m_s} = \frac{3}{4}\hbar^2 \chi_{m_s}$ $\hat{S}_z \chi_{m_s} = m_s \hbar \chi_{m_s}$

χ_+ $m_s = +\frac{1}{2}$

χ_- $m_s = -\frac{1}{2}$

So the total wavefunction of an electron in an atom is

$$\Psi_{n,l,m_l,m_s} = R_{nl}(r) Y_{lm_l}(\theta,\varphi) \chi_{m_s}$$

For complete characterization of the electron in a central force field 4 quantum numbers are necessary

$$\Psi_{n,l,m_l,m_s} = R_{nl}(r)\, Y_{l,m_l}(\theta,\varphi) \cdot \chi_{m_s}$$

Complete description of electron spin $\rightarrow$ relativistically invariant quantum mechanics (Dirac)

Coupling of the orbital ang. momentum and spin

Total angular momentum

$$\underline{J} = \underline{L} + \underline{S}$$

Possible values of J (possible states)

Addition rules for angular momenta:

$$\underline{J} = \underline{J}_1 + \underline{J}_2 \qquad J_z = J_{1z} + J_{2z} \rightarrow$$

$$J^2 = j(j+1)\hbar^2 \qquad J_z = m\hbar \qquad m = \pm j, \pm(j-1), \dots$$

$$m = m_1 + m_2$$

But J_1 and J_2 can have different relative directions

J can have different values

j from $(j_1 + j_2)$ to $(j_1 - j_2)$

parallel antiparallel

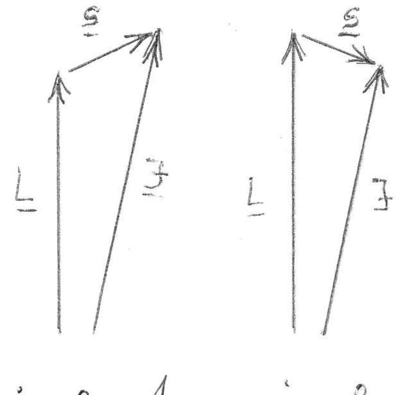
Orbital momentum and spin

$$\underline{J}_1 = \underline{L} \qquad \underline{J}_2 = \underline{S}$$

Possible values for $\underline{J} = \underline{J}_1 + \underline{J}_2$

$$j = l \pm \frac{1}{2}$$ (when $l = 0$ $j = \frac{1}{2}$ possible only)

l	0	1		2		3	
j	1/2	$\frac{1}{2}$	$\frac{3}{2}$	$\frac{3}{2}$	$\frac{5}{2}$	$\frac{5}{2}$	$\frac{7}{2}$
	$s_{1/2}$	$p_{1/2}$	$p_{3/2}$	$d_{3/2}$	$d_{5/2}$	$f_{5/2}$	$f_{7/2}$

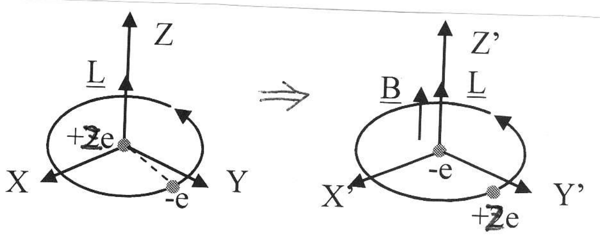


$j = l + \frac{1}{2}$ $\qquad$ $j = l - \frac{1}{2}$

up $\qquad$ down

Spin - orbit interaction

The spectral lines starting from the $l>0$ levels are doublets (e.g. D lines of Na /yellow/)
Connection with the 2 spin orientations?



From the coordinate system attached to the nucleus transfer to one attached to the "orbiting" electron (X', Y', Z') → the nucleus with charge $+Ze$ rotates around the electron → induces a magnetic field $\underline{B}$ ($\underline{B} \uparrow\uparrow \underline{L}$ since the charge is +)

In X', Y', Z' the electron is at rest → spin only → $\underline{M}_s$ magnetic moment only $\underline{M}_s \parallel \underline{S}$

Interaction energy $\underline{M}_s \cdot \underline{B} \sim \underline{S} \cdot \underline{L}$

$E_{SL} = a \cdot \underline{S}\,\underline{L}$ spin - orbit interaction

$E_{SL} \ll E_n$ (for normal energy levels)

$E = E_n + E_{SL} = E_n + a\,\underline{S}\,\underline{L}$

E_{SL} depends on the relative orientation of the two vectors → 2 possible states

Any state with a given l splits into 2 states (with small separation)
/except the s state/

$j = l + \frac{1}{2}$

$j = l - \frac{1}{2}$

In case of spin-orbit interaction the states are characterised by the following quantum numbers:

l, j, m where m is the eigenvalue of J_z

Selection rules for dipole transitions

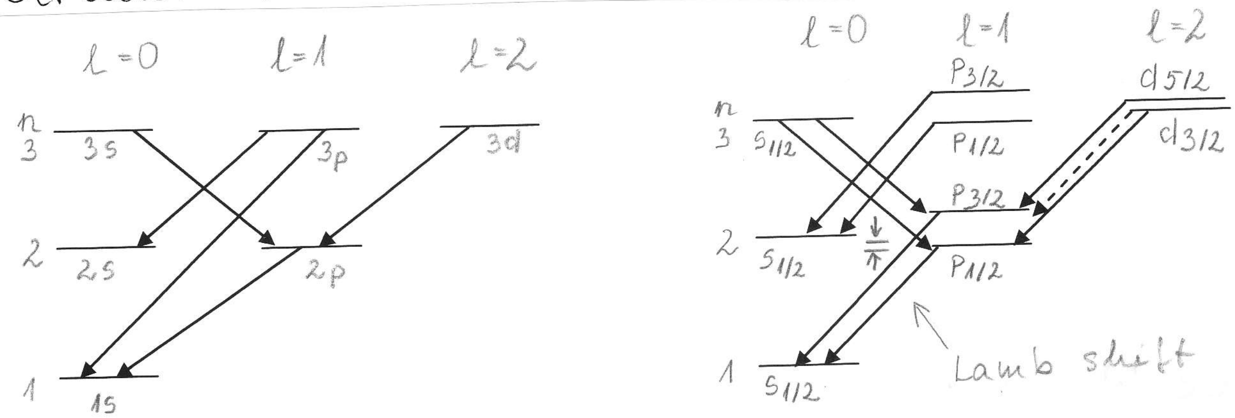
$\Delta l = \pm 1 \quad \Delta j = 0, \pm 1 \quad \Delta m = 0, \pm 1.$

$\Delta j = 0$ is weak, since it requires simultaneously:

$\Delta l = \pm 1$ and $\Delta s = \mp 1$ (low probability)

The spectrum of the H atom changes accordingly

Without L S interaction | With L S interaction



$\Delta l = \pm 1 \quad \Delta m_e = 0, \pm 1$

(Splittings in the figure are not to scale)

E.g. $\nu_{2p \to 1s} = 2{,}47 \cdot 10^{15}$ Hz

$\Delta\nu = \nu_{2P_{3/2} \to 1S_{1/2}} - \nu_{2P_{1/2} \to 1S_{1/2}} = 1{,}11 \cdot 10^{10}$ Hz

Fine structure of the spectrum

Identical j but different l: small shift

$\sim 10^{-1}$ fine structure

Lamb shift