Quantum mechanics / 5.

Angular momentum (26)
Schröd.-eq. in a central force field
H atom, atoms with 1 electr.

Angular momentum

Electron in an atom: energy, momentum are quantized
any other physical quantity?

Angular momentum $\underline{L} = \underline{r} \times \underline{p} = \underline{r} \times m\underline{v}$

In a central force field $\underline{L}$ is constant of motion
(no external torque!)

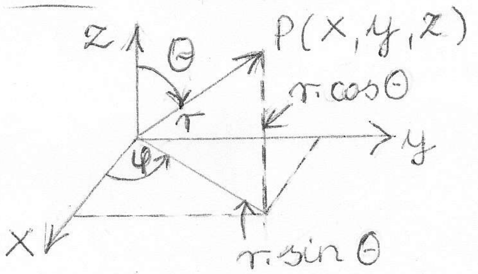
$\underline{L}$ is determined in quantum mechanics with
L_z and L^2 (classically: direction and absolute value)

$$\hat{L} = -i\hbar\, \underline{r} \times \underline{\nabla} = -i\hbar \begin{vmatrix} \underline{u}_x & \underline{u}_y & \underline{u}_z \\ x & y & z \\ \frac{\partial}{\partial x} & \frac{\partial}{\partial y} & \frac{\partial}{\partial z} \end{vmatrix}$$ (determinant

$$\to \hat{L}_z = -i\hbar\left(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right)$$ $\hat{L}_x, \hat{L}_y$ similar

In spherical coordinates: r, Θ, φ

$x = r\sin\Theta\cos\varphi$
$y = r\sin\Theta\sin\varphi$
$z = r\cos\Theta$



Let us write $\frac{\partial}{\partial\varphi}$ -

$$\frac{\partial}{\partial\varphi} = \frac{\partial x}{\partial\varphi}\frac{\partial}{\partial x} + \frac{\partial y}{\partial\varphi}\frac{\partial}{\partial y} + \frac{\partial z}{\partial\varphi}\frac{\partial}{\partial z}$$ but

$$\left.\begin{aligned} \frac{\partial x}{\partial\varphi} &= -r\sin\Theta\sin\varphi = -y \\ \frac{\partial y}{\partial\varphi} &= r\sin\Theta\cos\varphi = x \\ \frac{\partial z}{\partial\varphi} &= 0 \end{aligned}\right\}$$

$$\rightsquigarrow \frac{\partial}{\partial\varphi} = -y\frac{\partial}{\partial x} + x\frac{\partial}{\partial y}$$

$$\rightsquigarrow \hat{L}_z = -i\hbar\frac{\partial}{\partial\varphi}$$

Eigenvalue equation

$$\hat{L}_z \psi = L_z \psi \longrightarrow -i\hbar \frac{\partial \psi}{\partial \varphi} = L_z \psi$$

$\hbar = 10^{-34}$ Jsec (ang. mom.)

with $\frac{L_z}{\hbar} = m_e \longrightarrow \frac{\partial \psi}{\partial \varphi}\ i m_e \psi$

Solution: $\psi = C' e^{i m_e \varphi}$

But $\varphi \to \varphi + 2\pi$ ψ can not change $\rightsquigarrow$

$$e^{i 2\pi m_e} = 1 \rightsquigarrow m_e = 0, \pm 1, \pm 2 \ldots \text{ eigenvalues}$$

From normalization: $C' = \frac{1}{\sqrt{2\pi}} \rightsquigarrow$

$$\psi(\varphi) = \frac{1}{\sqrt{2\pi}} e^{i m_e \varphi} \quad \text{and } L_z = m_e \hbar \quad \hbar = 10^{-34} \text{ Jsec (ang. mom.)}$$

$\longrightarrow \hat{L}^2$?

$$\hat{L}^2 = \hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2$$

In spherical coordinates

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin\theta} \frac{\partial}{\partial \theta}\left(\sin\theta \frac{\partial}{\partial \theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2}{\partial \varphi^2} \right]$$

Eigenvalue equation:

$$\hat{L}^2 Y(\theta, \varphi) = L^2 Y(\theta, \varphi) \quad \text{substituting}$$

$$\frac{1}{\sin\theta} \frac{\partial}{\partial\theta}\left(\sin\theta \frac{\partial Y}{\partial \theta}\right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y}{\partial \varphi^2} + \frac{L^2}{\hbar^2} Y = 0$$

Solution: eigenvalues: $L^2 = \hbar^2 l(l+1)$ $l = 0, 1, 2, \ldots$

eigenfunctions: $Y_{e,m_e} = P_e^{m_e}(\cos\theta)\, e^{i m_e \varphi}$

Y_{e,m_e} $\hat{L}^2$ and $\hat{L}_z$ Legendre polynom of l-th order

Y_{e,m_e} are joint eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$

$$\hat{L}^2 Y_{l,m_e} = l(l+1)\hbar^2 Y_{l,m_e} \quad \hat{L}_z Y_{l,m_l} = m_l \hbar Y_{l\,m_l}$$

In a Coulomb field

Let the energy quantum number be $n \rightarrow$

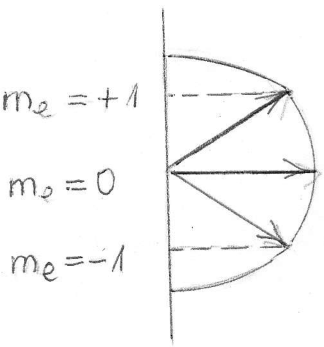
l can change between $0, \dots (n-1)$

The angle of the $\underline{L}$ vector with the z axis is discreet

$L_z = m_l \cdot \hbar$

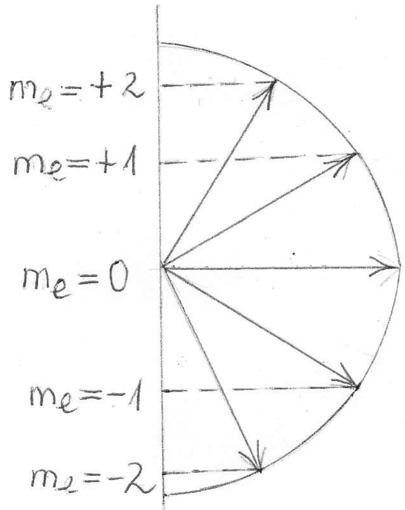
$m_l \leq l$ for a given l

$2l+1$ different m_l-s $\quad g = 2l+1 =$ degree of degeneracy



$l = 1$

p



$l = 2$

d

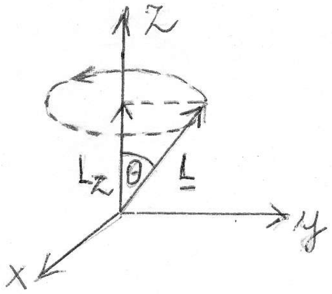
$l =$	0	1	2	3	4	5	...
denotion	s	p	d	f	g	h	
degree of degeneracy $(2l+1)$	1	3	5	7	9	11	

Only one component of the angular momentum vector $\underline{L}$ can be measured precisely

If L_z is known $\quad \Delta L_x \Delta L_y \geq \frac{\hbar}{2} L_z$

$\rightsquigarrow$ Direction of the angular momentum can not be precisely determined!

$|\underline{L}|$ and L_z are determined
$\underline{L}$ is precessing around
the z axes with a constant
ϑ angle



The Schrödinger equation in a central force field

$$E_p = E_p(\underline{r}) = E_p(r) \qquad \text{Coulomb } E_p(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r}$$

Schr. eq. $-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi + E_p(r)\psi = E\psi$

Transfer to spherical coordinates:

$$-\frac{\hbar^2}{2m}\left\{\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}+\frac{1}{r^2}\underbrace{\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\varphi^2}\right]}_{\frac{1}{\hbar^2}\hat{L}^2}\right\}\psi + E_p(r)\psi = E\psi$$

$$-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}-\frac{\hat{L}^2}{\hbar^2 r^2}\right)\psi + E_p(r)\psi = E\psi$$

Eigenfunctions of $\hat{L}^2$

$$\hat{L}^2 Y_{l,m_l} = l(l+1)\hbar^2 Y_{l,m_l}$$

using these

$$\psi = R(r)\, Y_{l,m_l}(\theta,\varphi)$$

we look for solutions in this form

Substituting

$$-\frac{\hbar^2}{2m}\left[\frac{d^2}{dr^2}+\frac{2}{r}\frac{d}{dr}-\frac{l(l+1)}{r^2}\right]R + E_p(r)R = E\cdot R$$

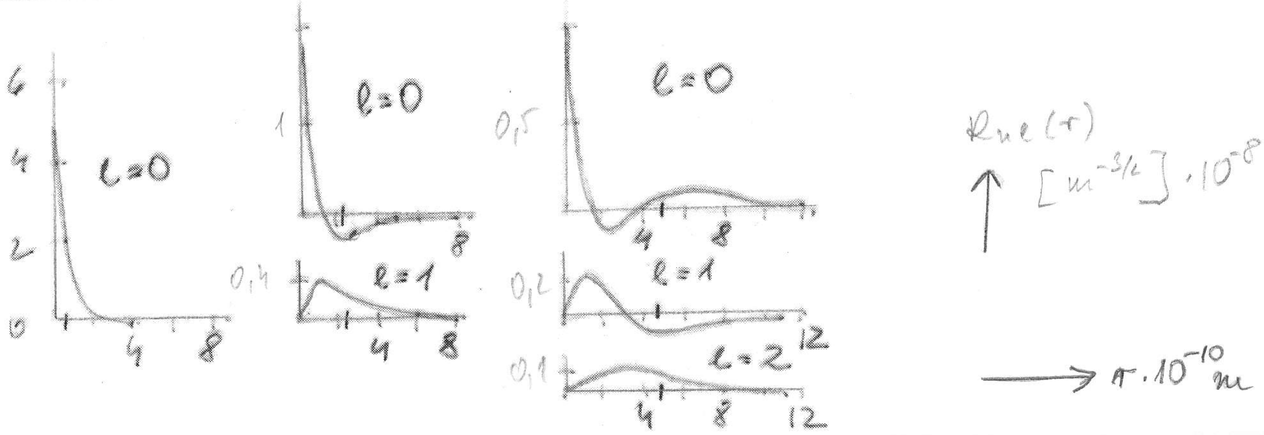
$R(r)$ is the radial part of the wavefunction

Trick: $R(r) = \frac{u(r)}{r} \rightarrow -\frac{\hbar^2}{2m}\frac{d^2 u}{dr^2} + \left[E_p + \frac{l(l+1)\hbar^2}{2mr^2}\right]u = Eu$

It is like a 1 dim. Schr. eq. $E_p^{eff} = E_p(r) + \frac{l(l+1)\hbar^2}{2mr^2}$

centrifugal potential

Radial part of the wavefunction (for a H atom) (real part)



s electrons ($l=0$) can get very close to the nucleus

p, d less because l increases

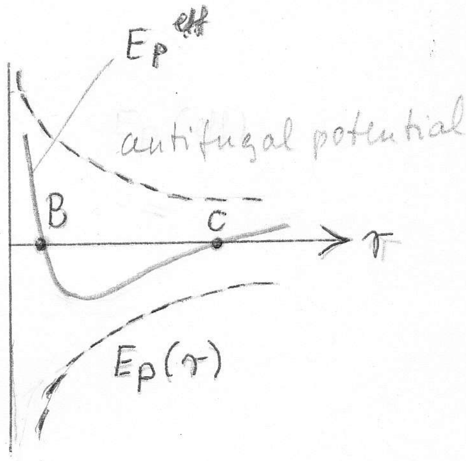
s orbit $l=0$ $E_p^{eff} = E_p$ - attractive

Centrifugal potential : repellent

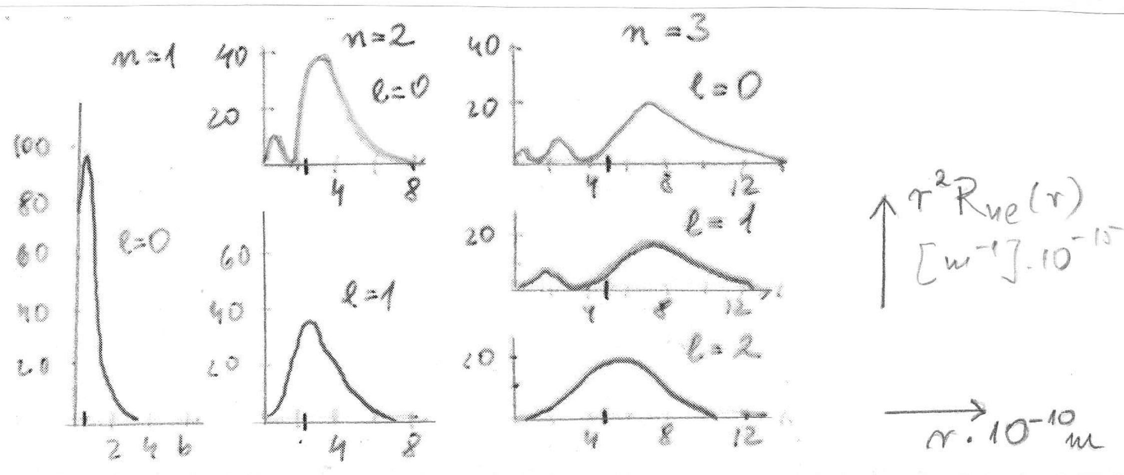
E_p^{eff} for $l>0$ sum of the two

→ oscillation between B and C

(does not get closer than C)



Radial distribution of probability (for a H atom)



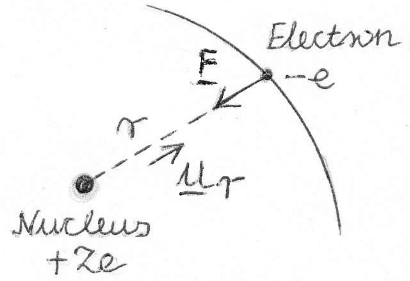
s electrons : sensitive to the internal structure of the nucleus

$l>0$, p, d electrons : less sensitive

Atoms size ~ 10^{-10} m (nucleus ~ 10^{-14} m)

- nucleus A (mass number) particles, of these
  Z (atomic number) protons } nucleons
  $N = A - Z$ neutrons
  nuclear charge: $+Ze$ \ Electromagnetic
- Z electrons with charge $-e$ / 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: $E_p(r) = -\dfrac{Ze^2}{4\pi\varepsilon_0 r}$ ⇝

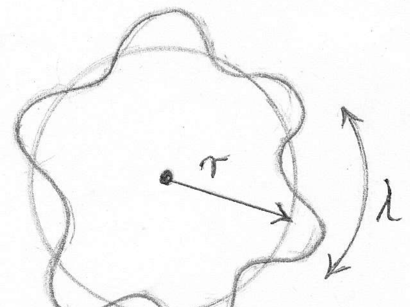
Schrödinger equation:

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

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

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

$\lambda = \frac{h}{p} \rightsquigarrow r \cdot p = L = \frac{nh}{2\pi} = n \cdot \hbar$ ang. mom.

Classically: centripetal force $\equiv$ Coulomb attraction

$$\frac{m_e \cdot v^2}{r} = \frac{Z \cdot e^2}{4\pi \epsilon_0 r^2} \qquad p = m_e \cdot v = \frac{n\hbar}{r} \rightsquigarrow v = \frac{n\hbar}{m_e \cdot r}$$

$$\rightsquigarrow r = \frac{n^2 \hbar^2 \epsilon_0}{\pi m_e Z e^2} = \frac{n^2}{Z} \cdot a_0 \qquad a_0 = \text{Bohr radius} = 5{,}3 \cdot 10^{-11} m$$

for the H atom $a_0 = r$ for $n=1$ (ground state)

The energy of the electron

$$E = E_{kin} + E_{pot} = \frac{1}{2} m_e v^2 - \frac{Ze^2}{4\pi\epsilon_0 r} = -\frac{1}{2} \frac{Ze^2}{4\pi\epsilon_0 r}$$

Substituting r

$$E = -\frac{m_e e^4 Z^2}{8\epsilon_0^2 h^2 n^2} = -\frac{R_\infty h c Z^2}{n^2} = -\frac{13{,}6 Z^2}{n^2} [eV]$$

$$R_\infty = \text{Rydberg constant } (m_{nucl} = \infty) = \frac{m_e e^4}{8\epsilon_0^2 h^3 c} = 1{,}1 \cdot 10^7 m^{-1}$$

Negative energies: bound states

Certain levels coincide?

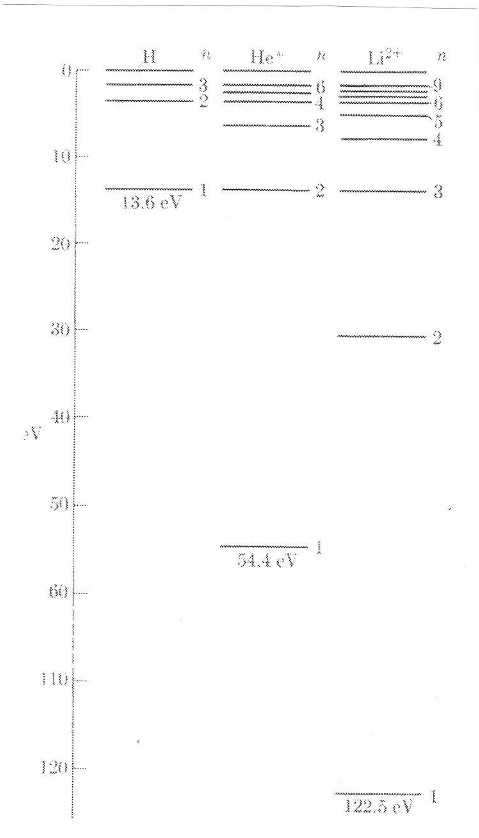
e.g. He^+ $n = 2, 4, 6$

Li^{2+} $n = 3, 6, 9$

No, because $m_{nucl} \neq \infty$

$$R = R_\infty \cdot \frac{\mu}{m_e}$$

$$\mu = \frac{m_e \cdot M_{nucl}}{m_e + M_{nucl}} = \text{reduced mass}$$



ionization energies!

Spectrum of the hydrogen atom

Measurement of radiation spectra: spectrometers

Energy differences between stationary energy states:

$$E_2 - E_1 = \left(-\frac{RhcZ^2}{n_2^2}\right) - \left(-\frac{RhcZ^2}{n_1^2}\right) = RhcZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

Bohr: $\nu = \dfrac{E_2 - E_1}{h}$ for the emitted or absorbed radiation

$$\nu = \frac{E_2 - E_1}{h} = RcZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 3{,}3 \cdot 10^{15} Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) [Hz]$$

This is the Balmer formula

Spectroscopy $\tilde{\nu} = \dfrac{\nu}{c} = \dfrac{1}{\lambda}$ wavenumber $[cm^{-1}]$

$$\tilde{\nu} = RZ^2\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) = 10^5 Z^2 \left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) [cm^{-1}]$$

Spectral lines

Series: joint lowest energy states

Balmer series: visible

Lyman series: UV

others: infra