Lecture 3
25.4.2023

Schrödinger's Hydrogen

- Today: **Quick** recap -> "Speed-talking"

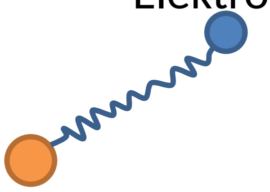
  (This will NOT be my regular speed

  during the rest of the semester!)
- Griffiths "Introduction to Quantum Mechanics"   Chapt. 4

- MIT Open Courseware

  https://ocw.mit.edu/courses/chemistry/5-61-physical-chemistry-fall-2013/lecture-notes/MIT5_61F13_Lecture19-20.pdf

Schrödinger's Hydrogen



Schrödinger Equation (SE)

$$i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\,\Psi \qquad (1.1)$$

The Hamiltonian operator $\hat{H}$ or simply "Hamiltonian" is very often also written without the the "hat": $\hat{H}$ = H

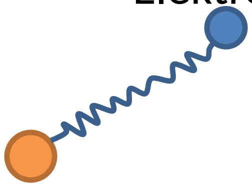
$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 + V(r) \qquad (1.2)$$

m_e= electron mass. Proton shall be infinitely heavy for now

The Laplacian is, in cartesian coordinates

$$\nabla^2 \equiv \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \qquad (1.3)$$

Time-independent SE



If V(**r**,t) = V(**r**) is **independent** of time, the solutions separate in spatial and time-dependent parts:

$$\Psi_n(\vec{r},t) \;=\; \Psi_n(\vec{r})\, e^{-iE_n t/\hbar} \qquad (1.4)$$

The spatial wave function satisfies time-**independent** SE:

$$-\frac{\hbar^2}{2m_e}\nabla^2\Psi_n \;+\; V\Psi_n \;=\; E_n\,\Psi_n \qquad (1.5)$$

or, in brief: $\hat{H}\,\Psi_n \;=\; E_n\,\Psi_n$

Spherical Laplacian

In the case of hydrogen-like systems, V(**r**) = $V(r) = \frac{Ze^2}{4\pi\epsilon_0}\frac{1}{r}$

= radially symmetric Coulomb potential.

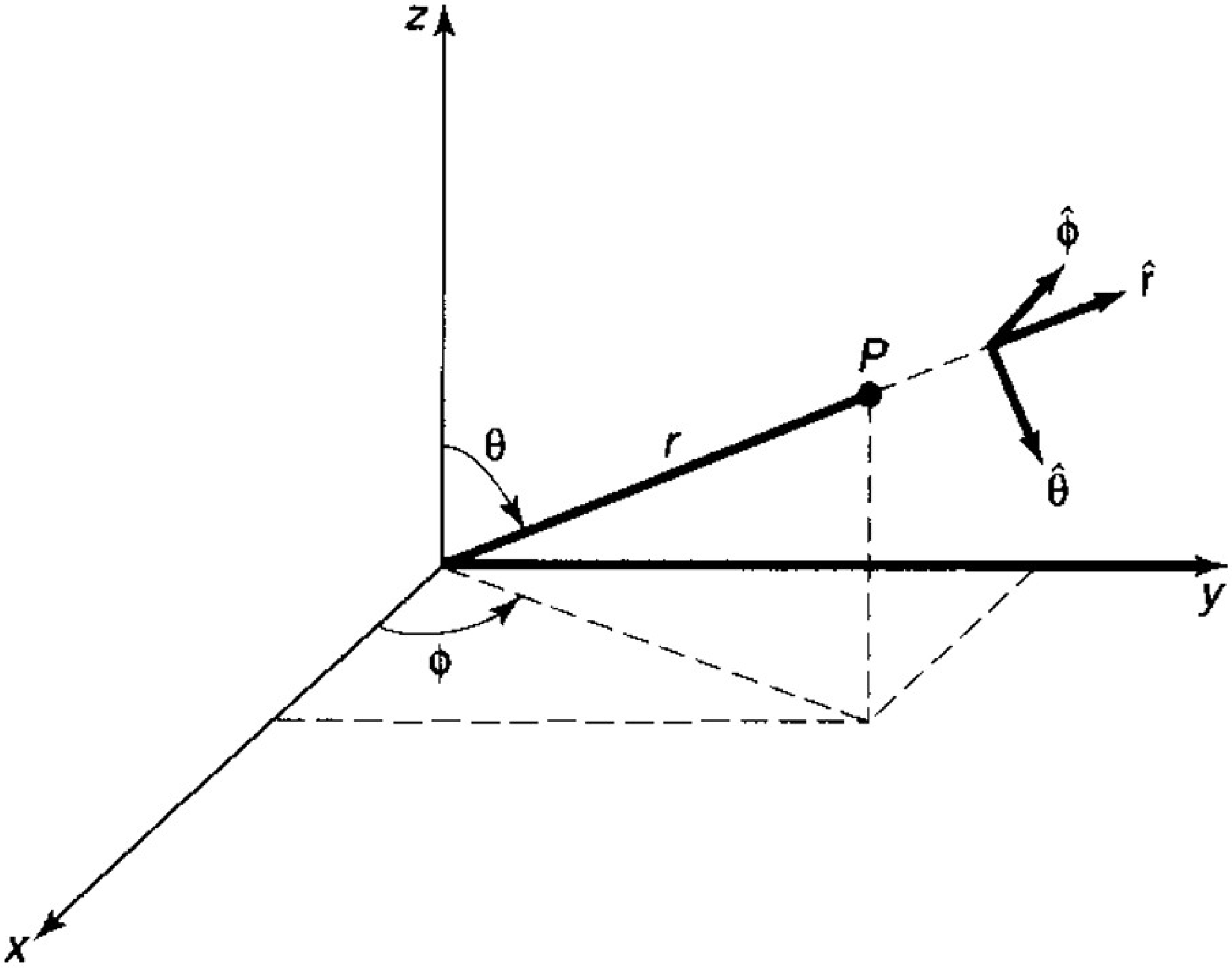
$$\vec{r} = (x, y, z) \rightarrow (r, \theta, \varphi)$$

Laplacian in spherical coordinates:

$$\begin{aligned}\nabla^2 &= \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) \\ &+ \frac{1}{r^2 sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial}{\partial\theta}\right) \\ &+ \frac{1}{r^2 sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right) \qquad (1.6)\end{aligned}$$

Spherical coordinates

Spherical coordinates:



Non-relativistic hydrogen

Time-independent SE in spherical coordinates, trying for the wave function

$$\Psi(r,\theta,\phi) \; = \; R(r)\,Y(\theta,\phi)$$

(separation of radial and angular part) yields

$$\left\{ \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2m_e r^2}{\hbar^2}\left[V(r) - E\right] \right\} \qquad (1.7)$$

$$+ \; \frac{1}{Y}\left\{ \frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta\frac{\partial Y}{\partial\theta}\right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} \right\} \; = \; 0$$

-> both parts must be **constants**

Non-relativistic hydrogen

Time-independen SE in spherical coordinates,
trying for the wave function

$$\Psi(r,\Theta,\phi) \; = \; R(r)\,Y(\Theta,\phi)$$

(separation of radial and angular part) yields

$$\left\{ \frac{1}{R}\frac{d}{dr}\left(r^2 \frac{dR}{dr} \right) - \frac{2m_{\mathrm{e}}r^2}{\hbar^2}\,[V(r)-E] \right\} \; = \; \ell(\ell+1)$$

$$\frac{1}{Y}\left\{ \frac{1}{sin\theta}\frac{\partial}{\partial\theta}\left(sin\theta \frac{\partial Y}{\partial\theta} \right) + \frac{1}{sin^2\theta}\frac{\partial^2 Y}{\partial\phi^2} \right\} \; = \; -\,\ell(\ell+1)$$

(1.8a,b)

The angular part

Multiply (1.8 b) by $Y \sin^2\theta$

again try separation of variables $Y(\theta,\phi) = \Theta(\theta)\ \Phi(\phi)$

$$\frac{1}{\Theta}\left[\sin\theta\frac{d}{d\theta}\left(\sin\theta\frac{d\Theta}{d\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2$$

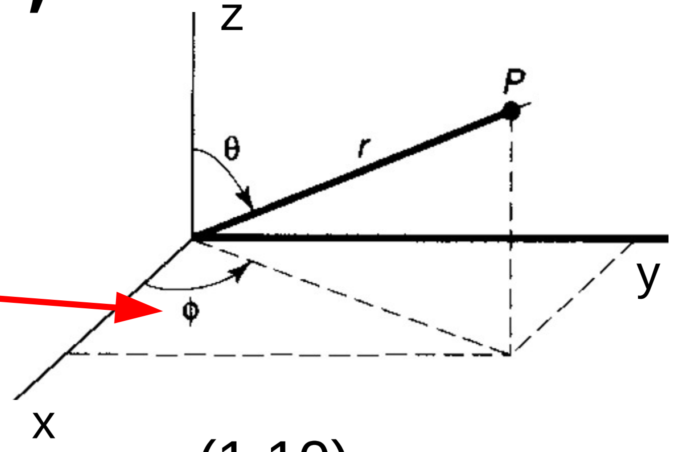
(1.9a,b)

$$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -\ m^2$$

2nd one is easy:

The angular part: ϕ, m

The easy one: $$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m^2$$



(1.10)

Solution: $$\Phi(\phi) = e^{i\,m\,\phi}$$

Note: Going from ϕ to $\phi + 2\pi$ gets you to the **same point in space**

-> $$\Phi(\phi + 2\pi) = \Phi(\phi)$$

or $$e^{2\pi i m} = 1$$

m = 0, ±1, ±2, ±3, …….

The angular part: Θ

$$\sin\theta \frac{d}{d\theta}\left(\sin\phi \frac{d\Theta}{d\theta}\right) \; + \; \left[\ell(\ell+1)\sin^2\theta \; - \; m^2\right]\Theta \; = \; 0$$

Solution: $$\Theta(\theta) \; = \; A\,P_\ell^m(\cos\theta)$$ (1.11)

Associated Legendre functions

$P_1^1 = \sin\theta$

$P_1^0 = \cos\theta$

$P_2^2 = 3\sin^2\theta$

$P_2^1 = 3\sin\theta\cos\theta$

$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$

$P_3^3 = 15\sin\theta(1 - \cos^2\theta)$

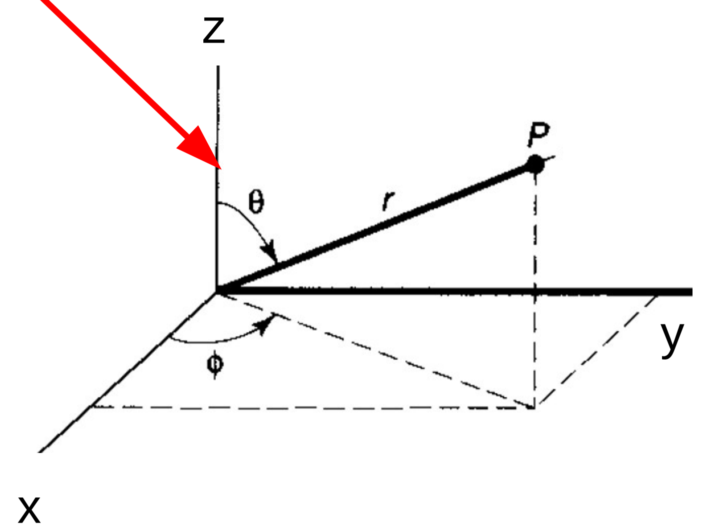
$P_3^2 = 15\sin^2\theta\cos\theta$

$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$

$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

z = “quantization axis”

(external field defines a special direction)



The angular part

See Griffiths for: some maths, normalizing the functions, looking at Rodriguez formula for Legendre, and make sure this Rodrigues formula makes sense)

Spherical Harmonics solve the angular part of our SE:

$$Y_\ell^m(\theta,\phi) \;=\; \epsilon\sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-|m|)!}{(\ell+|m|)!}}\,e^{im\phi}\,P_\ell^m(\cos\theta) \tag{1.12}$$

with $\epsilon \;=\; (-1)^m$ for m ≥0 and $\epsilon \;=\; 1$ for m<0

$$\ell = 0, 1, 2, ...$$

and $m \;=\; -\ell, -\ell+1, ... -1, 0, +1, \ell-1, \ell$

Spherical Harmonics

Table 4.2: The first few spherical harmonics, $Y_l^m(\theta, \phi)$.

$Y_0^0 = \left(\frac{1}{4\pi}\right)^{1/2}$	$Y_2^{\pm 2} = \left(\frac{15}{32\pi}\right)^{1/2} \sin^2\theta e^{\pm 2i\phi}$
$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$	$Y_3^0 = \left(\frac{7}{16\pi}\right)^{1/2} (5\cos^3\theta - 3\cos\theta)$
$Y_1^{\pm 1} = \mp\left(\frac{3}{8\pi}\right)^{1/2} \sin\theta e^{\pm i\phi}$	$Y_3^{\pm 1} = \mp\left(\frac{21}{64\pi}\right)^{1/2} \sin\theta(5\cos^2\theta - 1)e^{\pm i\phi}$
$Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$	$Y_3^{\pm 2} = \left(\frac{105}{32\pi}\right)^{1/2} \sin^2\theta\cos\theta e^{\pm 2i\phi}$
$Y_2^{\pm 1} = \mp\left(\frac{15}{8\pi}\right)^{1/2} \sin\theta\cos\theta e^{\pm i\phi}$	$Y_3^{\pm 3} = \mp\left(\frac{35}{64\pi}\right)^{1/2} \sin^3\theta e^{\pm 3i\phi}$

The radial part

$$\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2mr^2}{\hbar^2}\left[V(r) - E\right]R \;=\; \ell(\ell+1)\,R$$

(1.8a) = (1.13)

Change variables: *u(r) = r R(r)*

radial SE

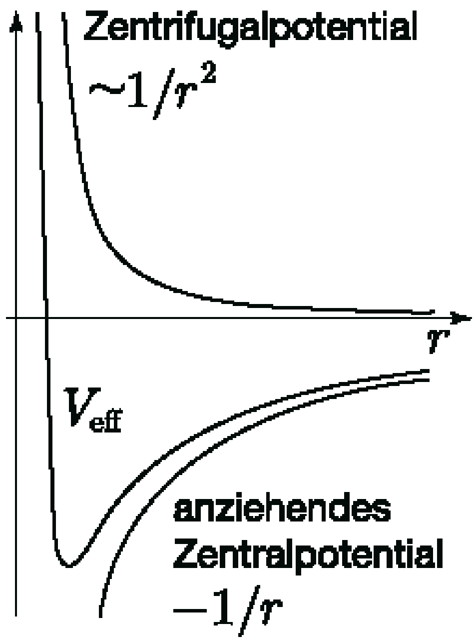
$$-\frac{\hbar^2}{2m}\frac{d^2u}{dr^2} + \left[V \,+\, \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right]u \;=\; E\,u \qquad (1.14)$$

is like 1D-SE plus extra term: centrifugal barrier

Radial part of the wave function

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial r^2}+\frac{2}{r}\frac{\partial}{\partial r}\right)+\underbrace{\frac{\hbar^2 l(l+1)}{2mr^2}-\frac{e^2}{r}}\right]R(r)=ER(r)$$

effective potential:
centrifugal barrier + Coulomb!



Physics behind this:

- l=0 – no barrier
- increasing barrier with increasing l -> electron moves closer to the nucleus $\langle r\rangle_{l+1} < \langle r\rangle_l$
- E = binding energy;
  if energy goes into angular momentum, the electron has to come closer to the nucleus to have the same binding for the same total energy.

Hydrogen a la Schrödinger

so far: completely general for any spherical potential

H atom: Coulomb potential
(for Z=1)

$$V(r) = \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}$$

(... maths... -> Griffiths)

Bohr formula

$$E_n = -\left[\frac{m_e}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}$$ n=1, 2, 3, ...

= **-13.6 eV** / n^2

Bohr radius $$a_B = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$$ = 0.529 x 10^{-10} m

Radial part of H wave function

(...) gets you to Laguerre polynomials..., see Griffiths

Table 4.6: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$$

$$R_{40} = \frac{1}{4}a^{-3/2}\left(1 - \frac{3}{4}\frac{r}{a} + \frac{1}{8}\left(\frac{r}{a}\right)^2 - \frac{1}{192}\left(\frac{r}{a}\right)^3\right)\exp(-r/4a)$$

$$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}}a^{-3/2}\left(1 - \frac{1}{4}\frac{r}{a} + \frac{1}{80}\left(\frac{r}{a}\right)^2\right)\frac{r}{a}\exp(-r/4a)$$

Radial part of H wave function

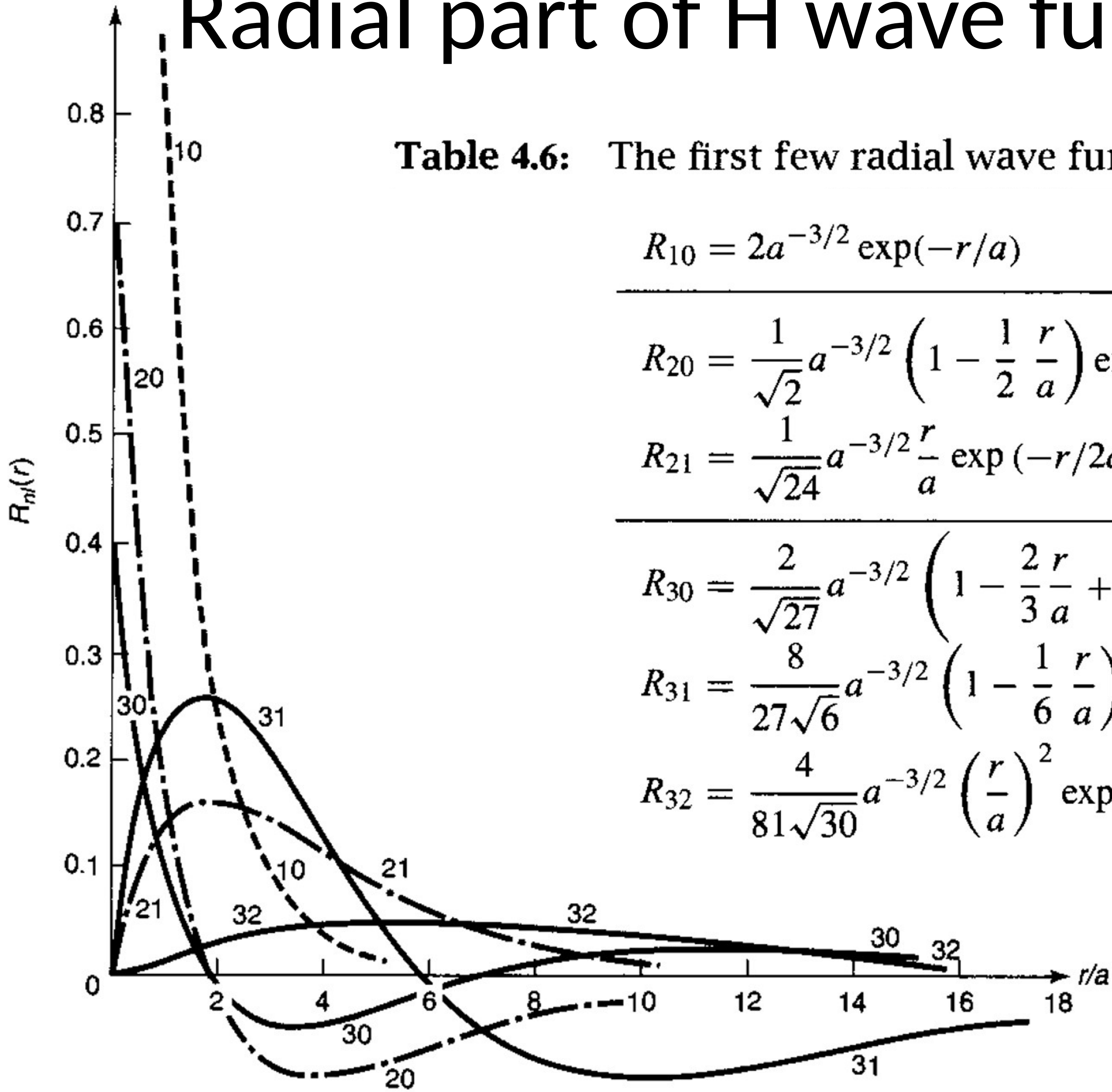


Table 4.6: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

$$R_{10} = 2a^{-3/2}\exp(-r/a)$$

$$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1 - \frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$$

$$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$$

$$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$$

$$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1 - \frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$$

$$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$$

Figure 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

Schrödinger wave function for H

$$\Psi_{n\ell m} = \sqrt{\left(\frac{2}{na_B}\right)^3 \frac{(n-\ell-1)!}{2n[(n+l)!]^3}} e^{-r/na_B}$$

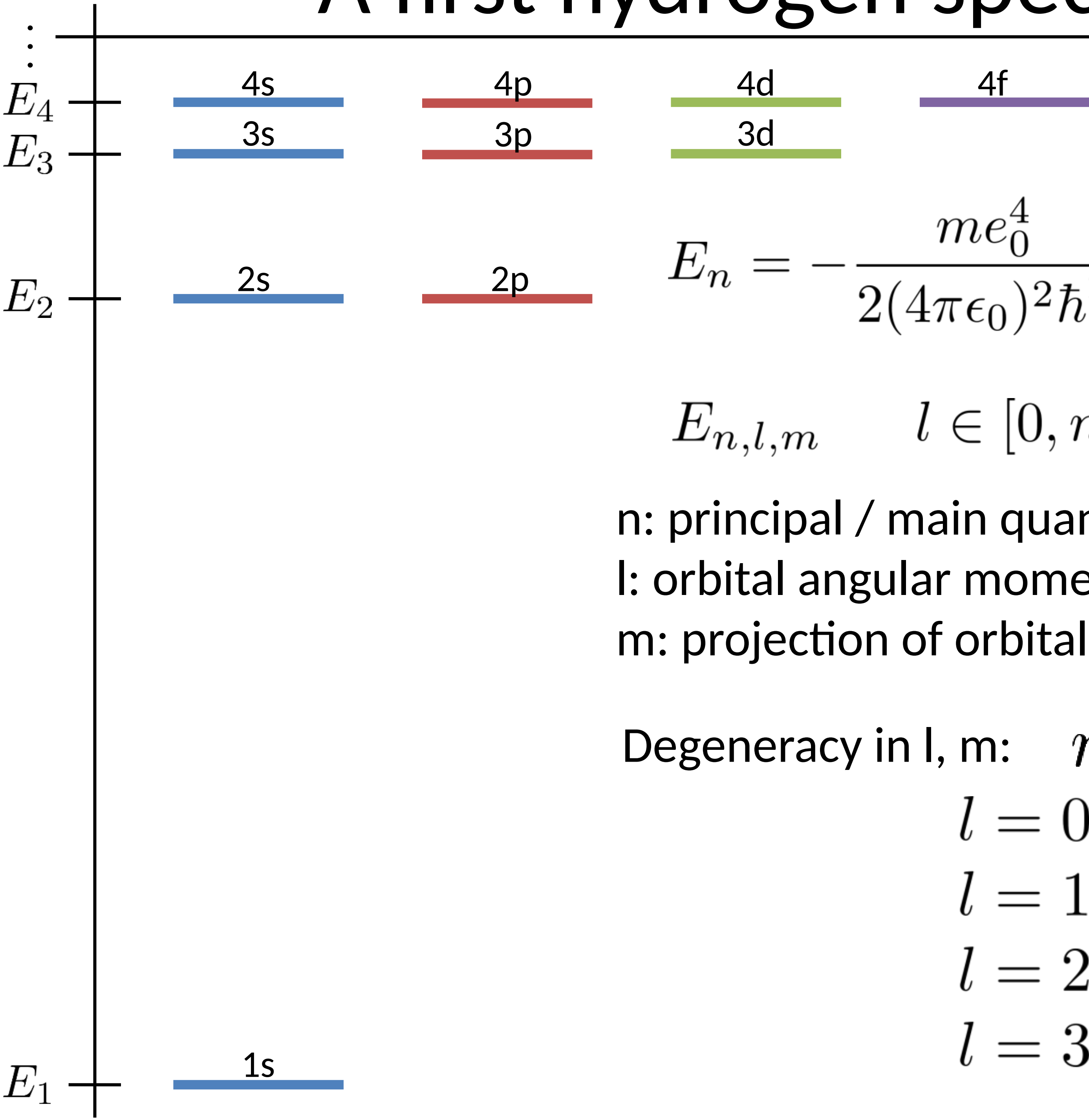
$$\times \left(\frac{2r}{na_B}\right)^{\ell} L_{n-\ell-1}^{2\ell+1}\left(\frac{2r}{n\,a_B}\right) \times Y_\ell^m(\theta,\phi)$$

$$n = 1, 2, 3, ...$$

$$\ell = 0, 1, ...n-1$$

$$m = -\ell, ...\ell$$

A first hydrogen spectrum



$$E_n = -\frac{me_0^4}{2(4\pi\epsilon_0)^2\hbar^2} \cdot \frac{1}{n^2}, n \in 1, 2, 3, 4, \ldots$$

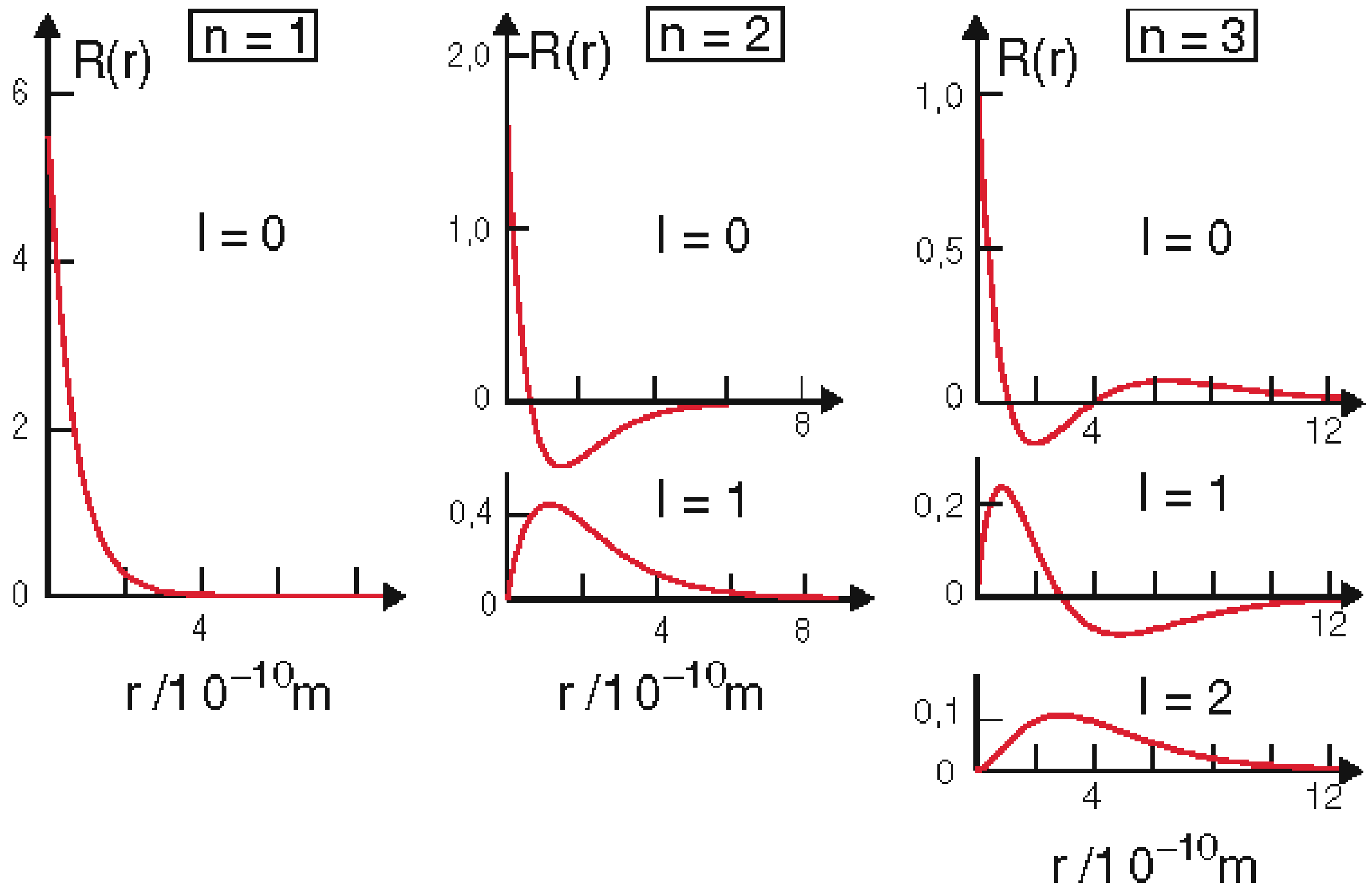
$$E_{n,l,m} \qquad l \in [0, n-1], m \in [-l, l]$$

n: principal / main quantum number
l: orbital angular momentum quantum number
m: projection of orbital angular momentum

Degeneracy in l, m: n^2

$$l = 0 \quad \leftrightarrow \quad s$$
$$l = 1 \quad \leftrightarrow \quad p$$
$$l = 2 \quad \leftrightarrow \quad d$$
$$l = 3 \quad \leftrightarrow \quad f$$

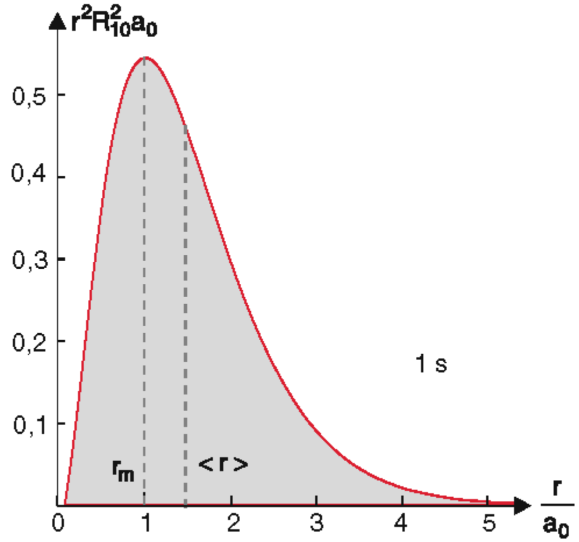
Again: Radial part of the wave function

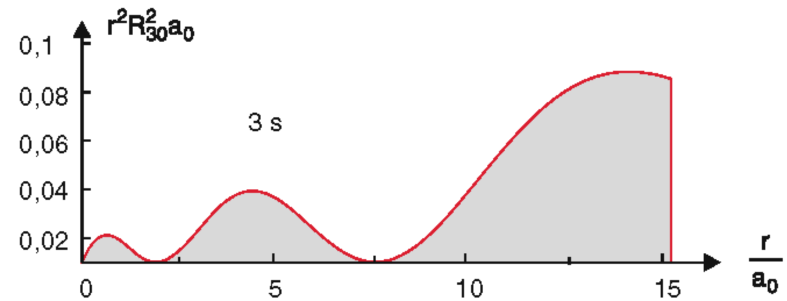


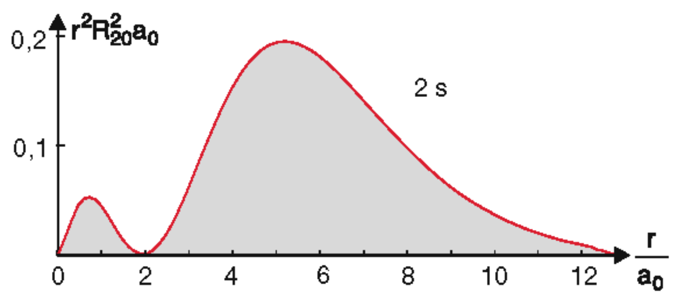
R(r) are interesting, but probability densities are more intuitive

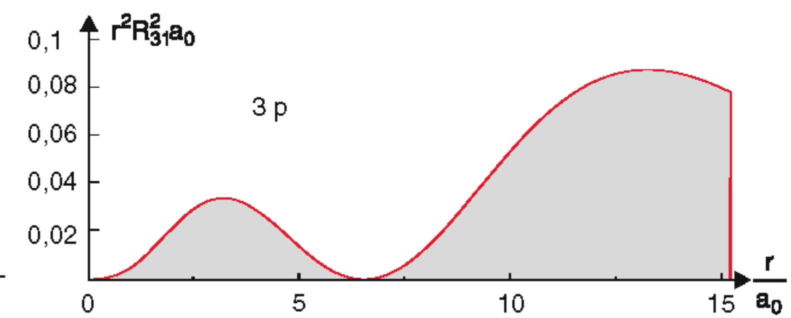
probability density $r^2|R(r)|^2$

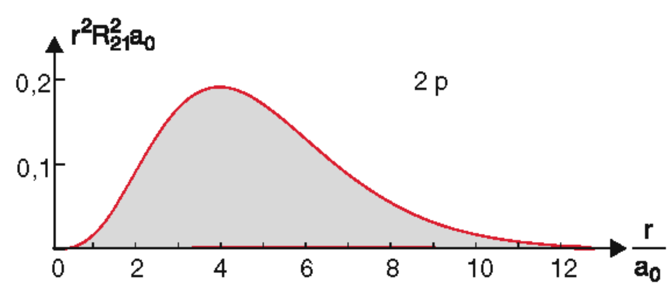
$$(d^3x \to r^2 dr d\varphi \sin\theta d\theta)$$

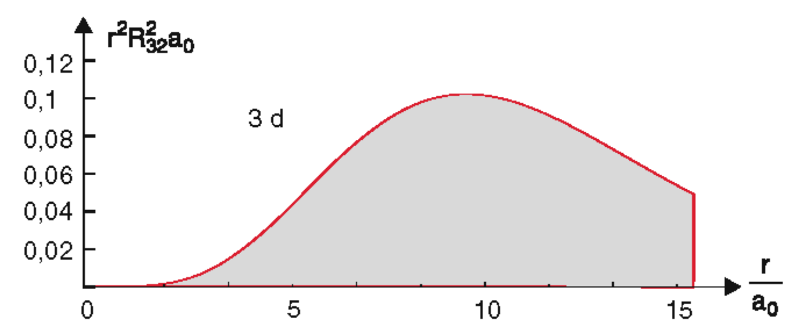












Some properties

- The **most probable distance** for the maximally possible angular momentum **l=n-1,** that is: the maximum of the probability density is:

$$r_n = n^2 a_B$$ “n-squared times the Bohr radius”

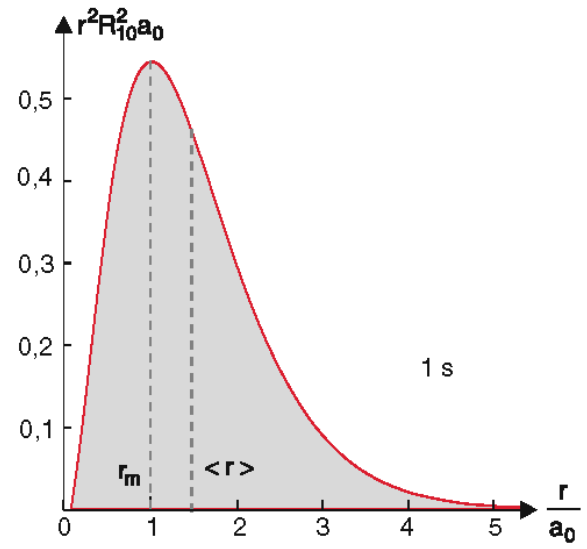
- The **mean distance** is:

$$\langle r \rangle_{n,l} = \int_0^\infty r |R_{n,l}(r)|^2 r^2 dr = a_B \left(\frac{3}{2} n^2 - \frac{l(l+1)}{2} \right)$$

Example: n=1

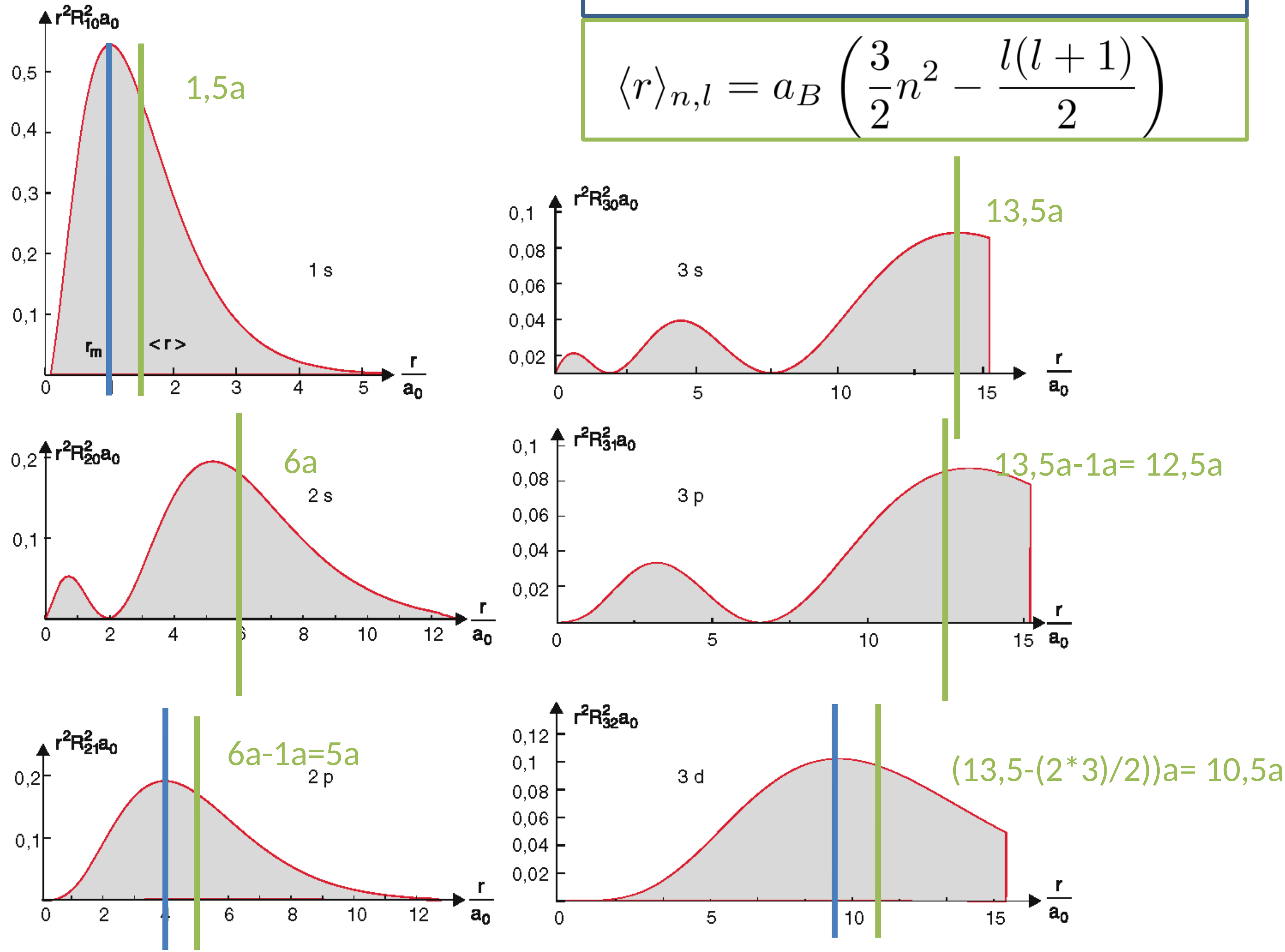
$$r_1 = a_B$$

$$\langle r \rangle_{1,0} = \frac{3}{2} a_B$$



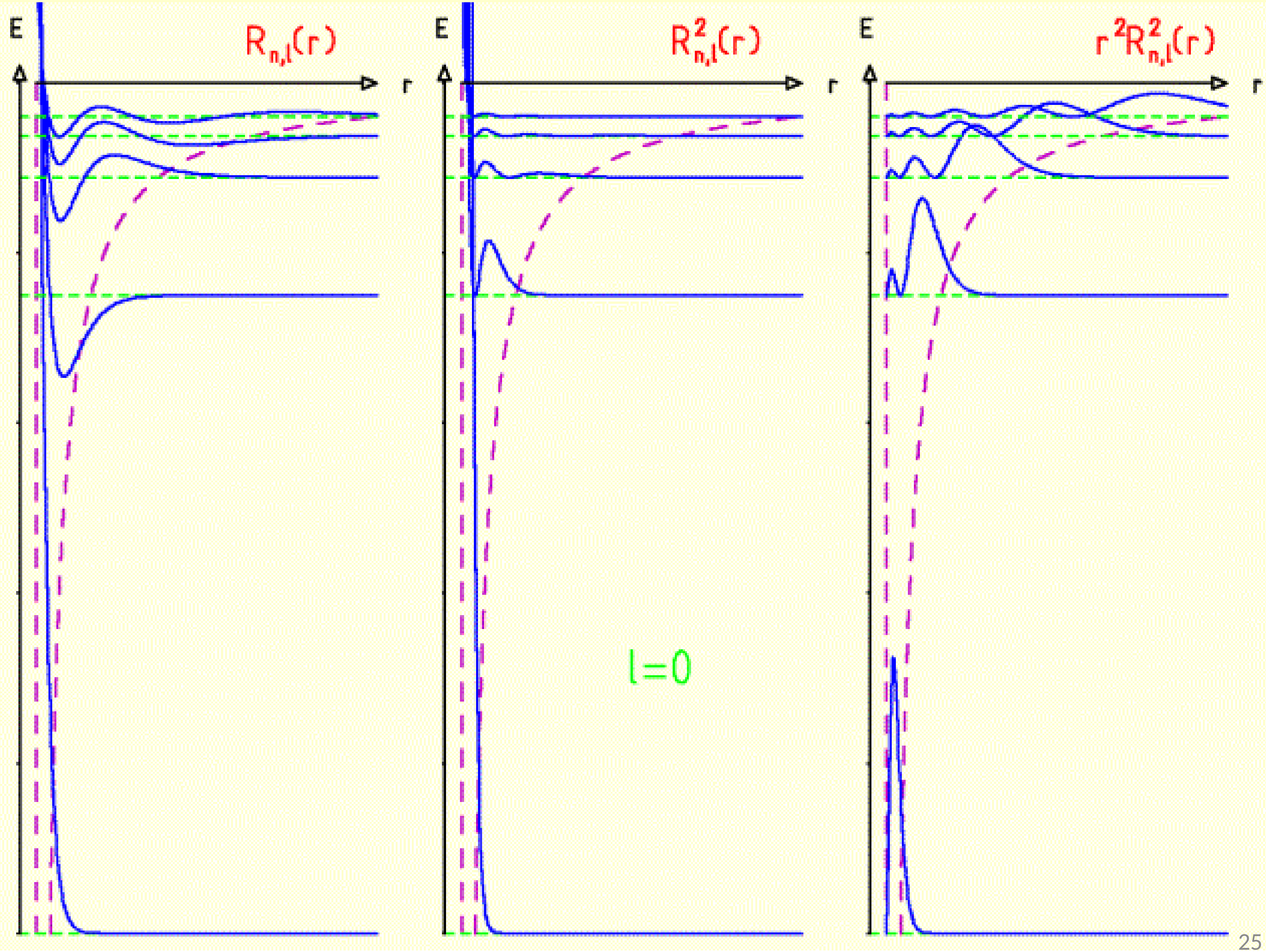
$$r_n = n^2 a_B \quad @l = l_{\max} = n-1$$

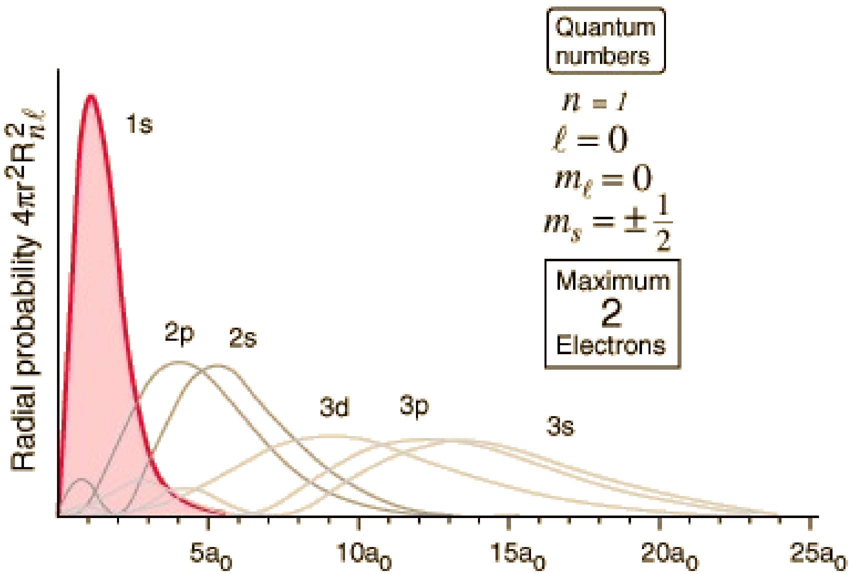
$$\langle r \rangle_{n,l} = a_B \left(\frac{3}{2} n^2 - \frac{l(l+1)}{2} \right)$$

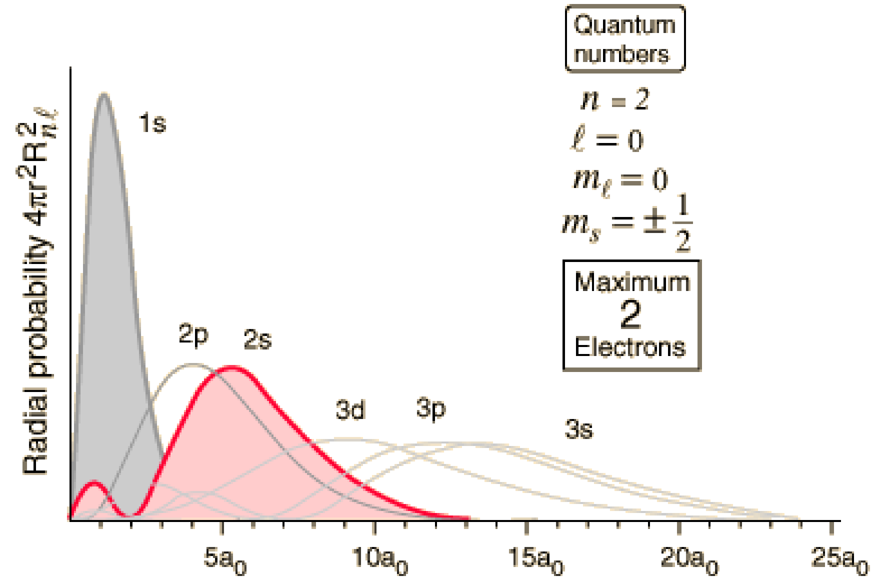


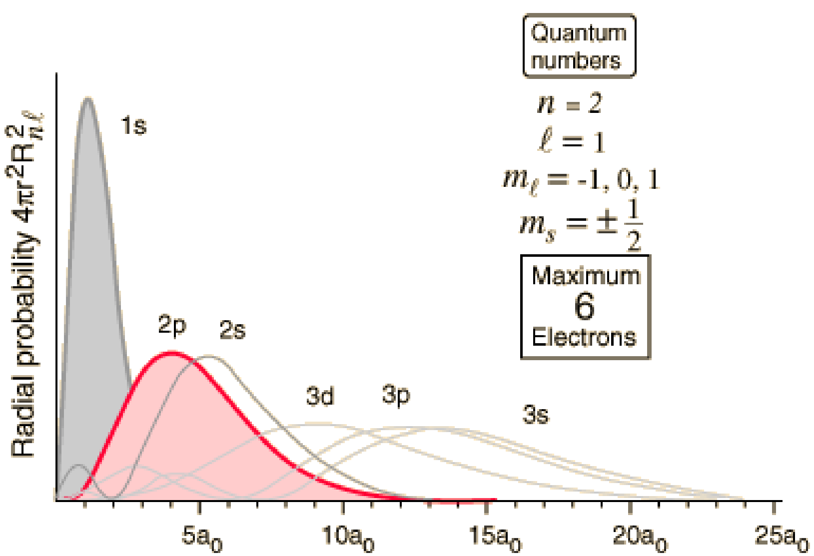
This rough systematic is worth memorizing

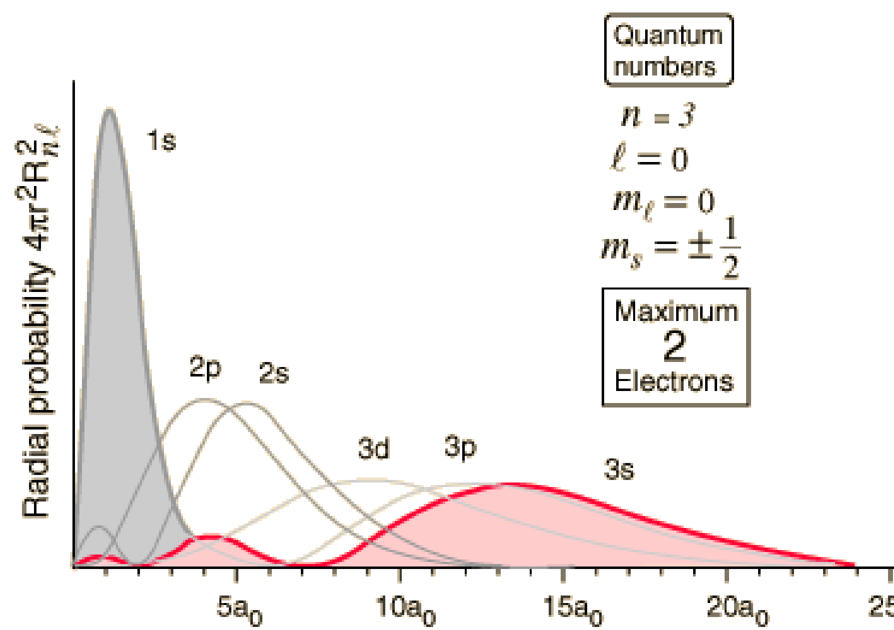
Die Eigenzustände des Elektrons im Wasserstoffatom (Radialanteil R)




Quantum numbers
n = 1
ℓ = 0
$m_\ell = 0$
$m_s = \pm\frac{1}{2}$
Maximum 2 Electrons
Radial probability $4\pi r^2 R_{n\ell}^2$
1s
2p
2s
3d
3p
3s
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$

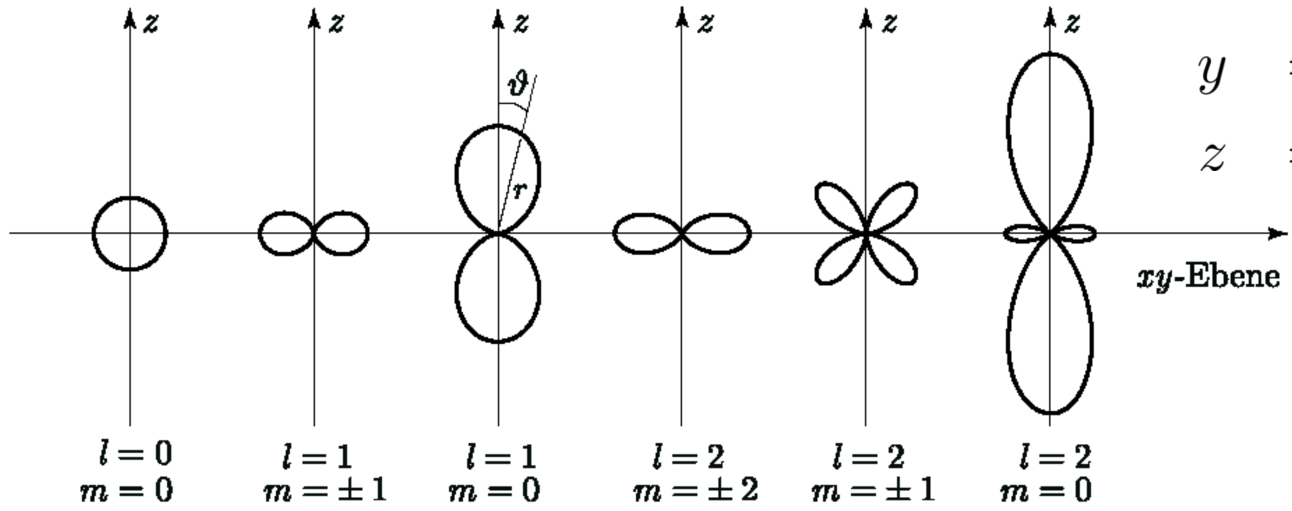

Quantum numbers
n = 2
ℓ = 0
$m_\ell = 0$
$m_s = \pm\frac{1}{2}$
Maximum 2 Electrons
Radial probability $4\pi r^2 R_{n\ell}^2$
1s
2p
2s
3d
3p
3s
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$


Quantum numbers
n = 2
ℓ = 1
$m_\ell = -1, 0, 1$
$m_s = \pm\frac{1}{2}$
Maximum 6 Electrons
Radial probability $4\pi r^2 R_{n\ell}^2$
1s
2p
2s
3d
3p
3s
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$


Quantum numbers
n = 3
ℓ = 0
$m_\ell = 0$
$m_s = \pm\frac{1}{2}$
Maximum 2 Electrons
Radial probability $4\pi r^2 R_{n\ell}^2$
1s
2p
2s
3d
3p
3s
$5a_0$
$10a_0$
$15a_0$
$20a_0$
$25a_0$

Winkelanteil der Wellenfunktion $Y_{lm}(\theta,\varphi)$

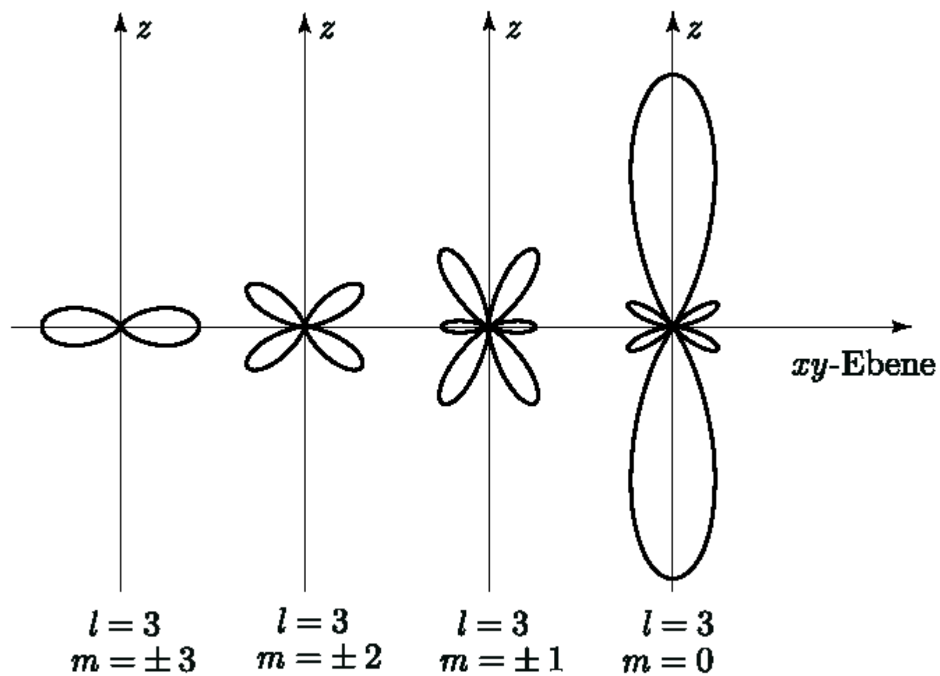
$$\begin{aligned} x &= r\cdot\sin\theta\cos\varphi \\ y &= r\cdot\sin\theta\sin\varphi \\ z &= r\cdot\cos\theta \end{aligned}$$



Alles rotations-
symmetrisch um z

d.h. die Länge des Vektors r

$r = |Y_{lm}(\vartheta,\varphi)|^2$



Winkelanteil der Wellenfunktion $Y_{lm}(\theta, \varphi)$

$$Y_{00} = \frac{1}{\sqrt{4\pi}}$$

$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos\theta \qquad Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin\theta e^{i\varphi}$$

$$Y_{20} = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1) \quad Y_{21} = -\sqrt{\frac{15}{8\pi}} \sin\theta \cos\theta e^{i\varphi} \quad Y_{22} = \sqrt{\frac{15}{32\pi}} \sin^2\theta e^{2i\varphi}$$

$$|Y_{lm}(x, y, z)|^2$$