

Lecture 3

27.10.2021

Schrödinger's Hydrogen

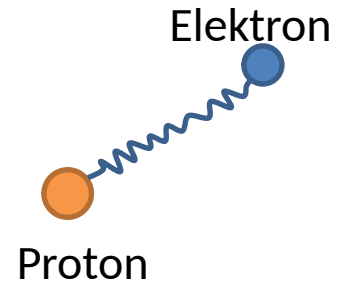
- Today: **Quick** recap -> “Speed-talking”
(This will NOT be my regular speed during the rest of the semester!)
- Griffiths “Introduction to Quantum Mechanics” Chapt. 4
- MIT Open Courseware

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)

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



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

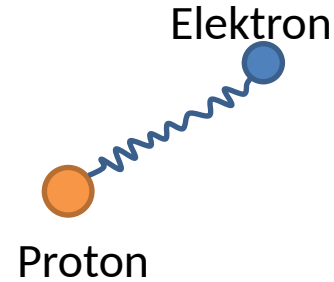
$$\hat{H} = -\frac{\hbar^2}{2m_e} \nabla^2 + V(r) \quad (1.2)$$

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

The Laplacian is, in cartesian coordinates

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

Time-independent SE



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

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

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

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

or, in brief:

$$\hat{H} \Psi_n = E_n \Psi_n$$

Spherical Laplacian

In the case of hydrogen-like systems, $V(\mathbf{r}) = V(r) = \frac{Ze^2}{4\pi\epsilon_0} \frac{1}{r}$
= radially symmetric Coulomb potential.

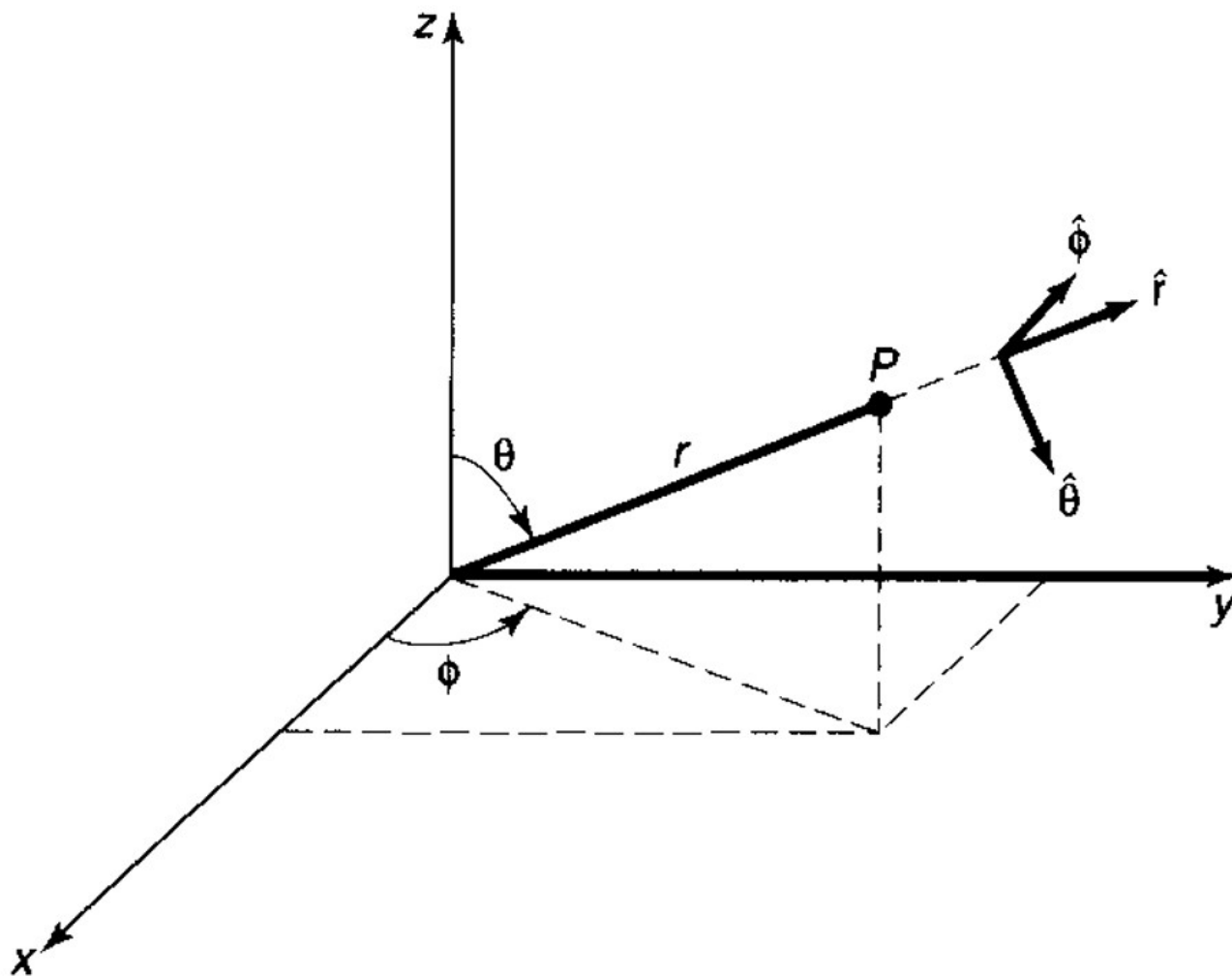
$$\vec{r} = (x, y, z) \rightarrow (r, \theta, \varphi)$$

Laplacian in spherical coordinates:

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

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

$$\left\{ \frac{1}{R} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) - \frac{2m_e r^2}{\hbar^2} [V(r) - E] \right\} \quad (1.7)$$
$$+ \frac{1}{Y} \left\{ \frac{1}{\sin\theta} \frac{\partial}{\partial\theta} \left(\sin\theta \frac{\partial Y}{\partial\theta} \right) + \frac{1}{\sin^2\theta} \frac{\partial^2 Y}{\partial\phi^2} \right\} = 0$$

-> both parts must be **constants**

Non-relativistic hydrogen

Time-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

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

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

(1.8a,b)

The angular part

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

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

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

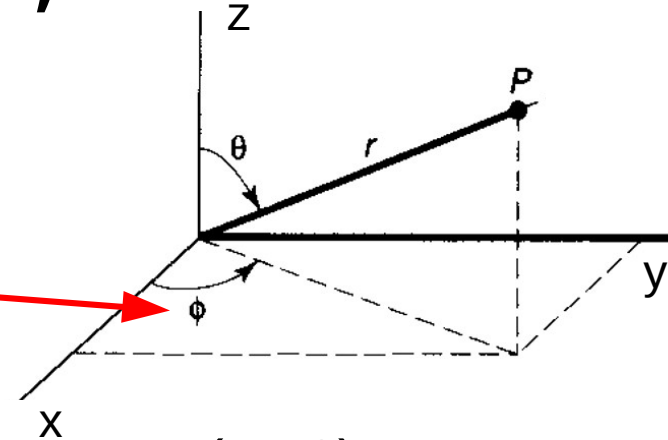
$$\frac{1}{\Phi} \frac{d^2 \Phi}{d\phi^2} = -m^2 \quad (1.9a,b)$$

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**

$$\rightarrow \Phi(\phi + 2\pi) = \Phi(\phi)$$

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

$$m = 0, \pm 1, \pm 2, \pm 3, \dots$$

The angular part: Θ

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

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

Associated Legendre functions

$$P_1^1 = \sin \theta$$

$$P_1^0 = \cos \theta$$

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

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

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

$$P_3^3 = 15 \sin^3 \theta$$

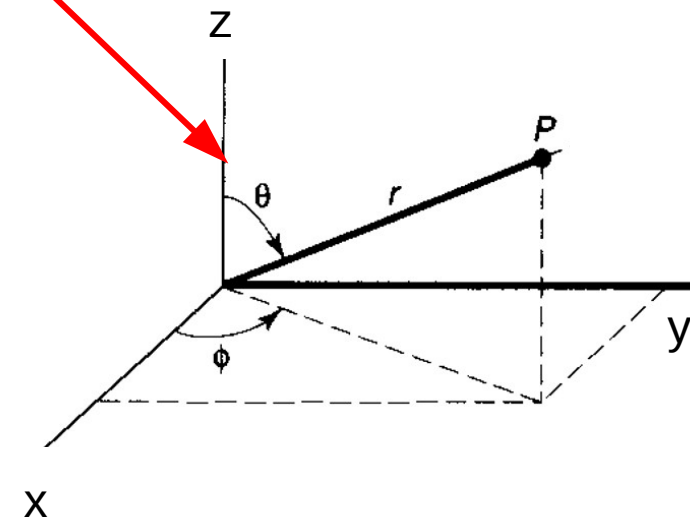
$$P_3^2 = 15 \sin^2 \theta \cos \theta$$

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

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

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:

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

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

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

and $m = -\ell, -\ell + 1, \dots, -1, 0, +1, \ell - 1, \ell$

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

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

(1.8a) = (1.13)

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

radial SE

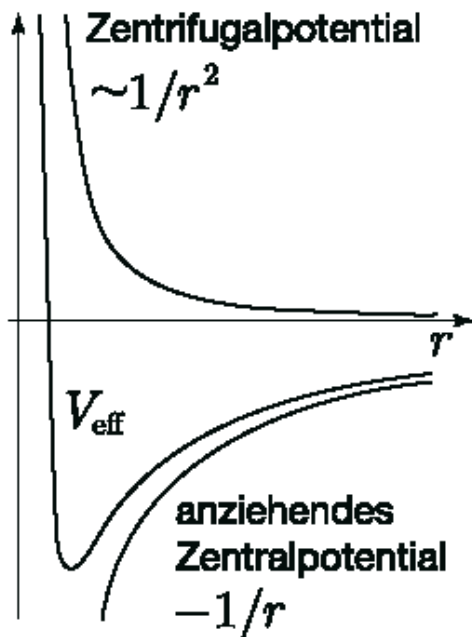
$$-\frac{\hbar^2}{2m} \frac{d^2 u}{dr^2} + \left[V + \frac{\hbar^2}{2m} \frac{\ell(\ell + 1)}{r^2} \right] u = E u \quad (1.14)$$

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

$$E_n = - \left[\frac{m_e}{2\hbar^2} \left(\frac{e^2}{4\pi\epsilon_0} \right)^2 \right] \frac{1}{n^2} \quad n=1, 2, 3, \dots$$
$$= \quad \mathbf{-13.6 \text{ eV}} / n^2$$

Bohr radius

$$a_B = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2} = 0.529 \times 10^{-10} \text{ m}$$

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, $R_{nl}(r)$.

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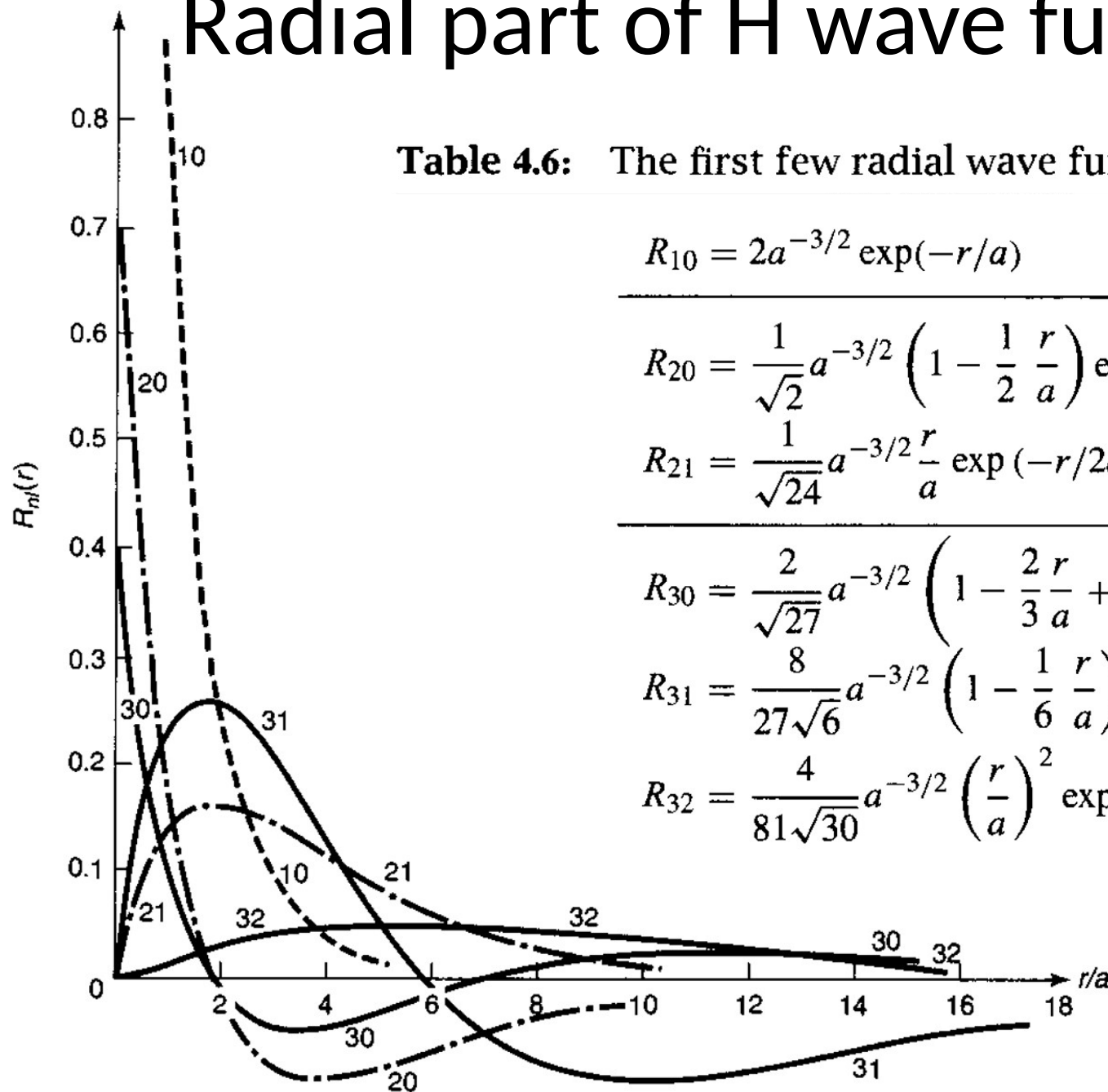


Figure 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

Schrödinger wave function for H

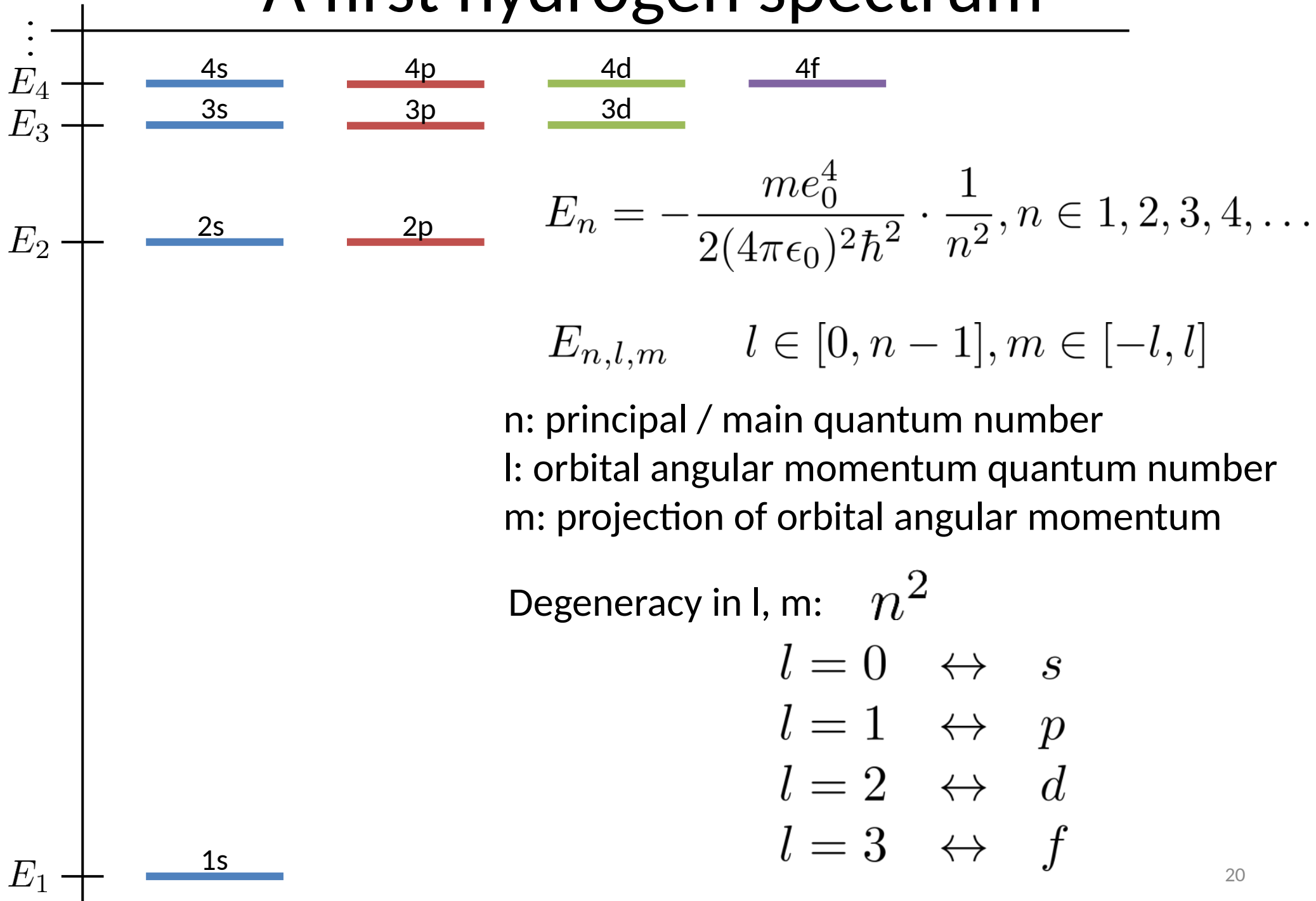
$$\Psi_{n\ell m} = \sqrt{\left(\frac{2}{na_B}\right)^3 \frac{(n-\ell-1)!}{2n[(n+\ell)!]^3}} e^{-r/na_B} \\ \times \left(\frac{2r}{na_B}\right)^\ell L_{n-\ell-1}^{2\ell+1} \left(\frac{2r}{na_B}\right) \times Y_\ell^m(\theta, \phi)$$

$$n = 1, 2, 3, \dots$$

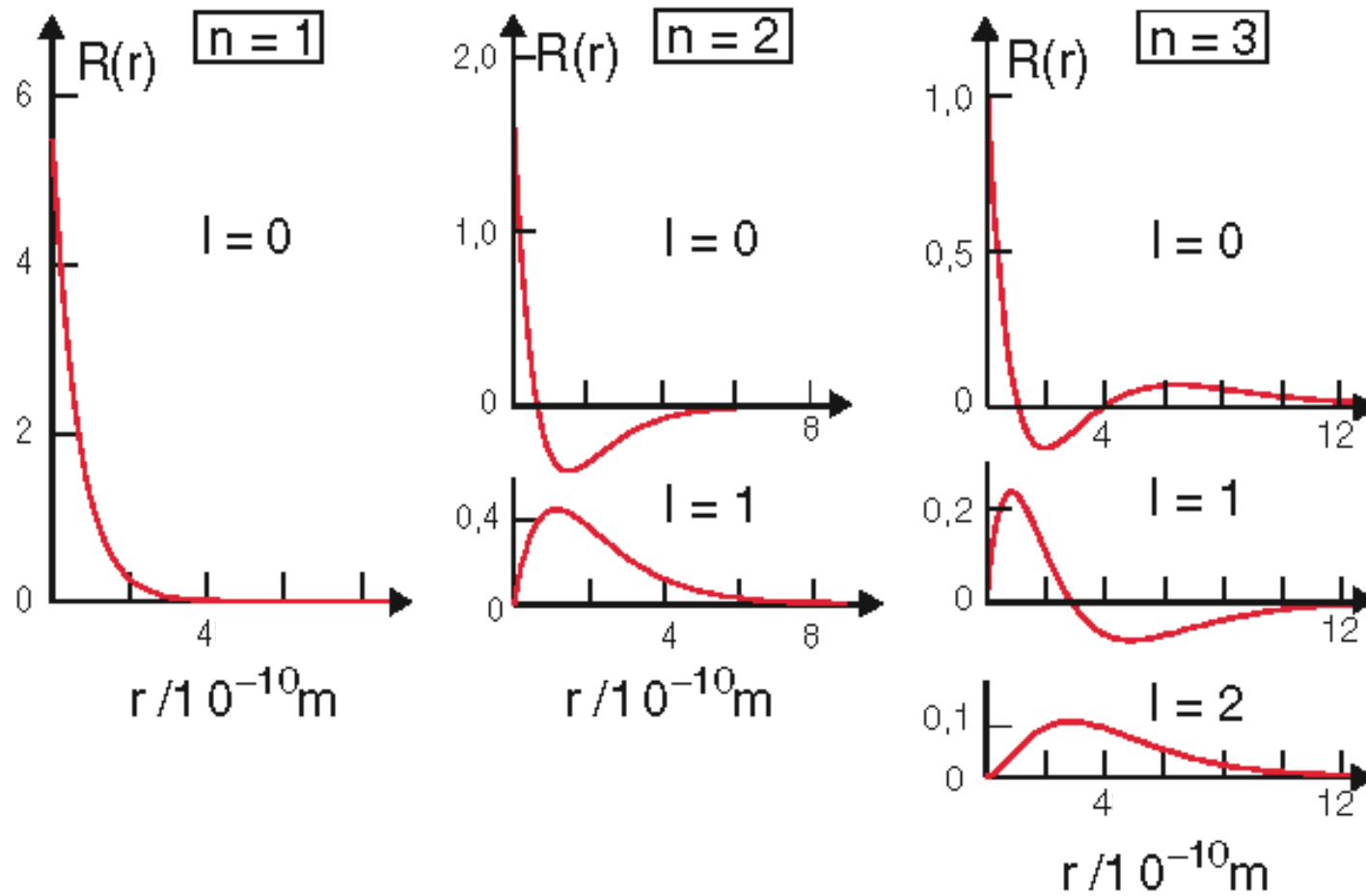
$$\ell = 0, 1, \dots, n-1$$

$$m = -\ell, \dots, \ell$$

A first hydrogen spectrum



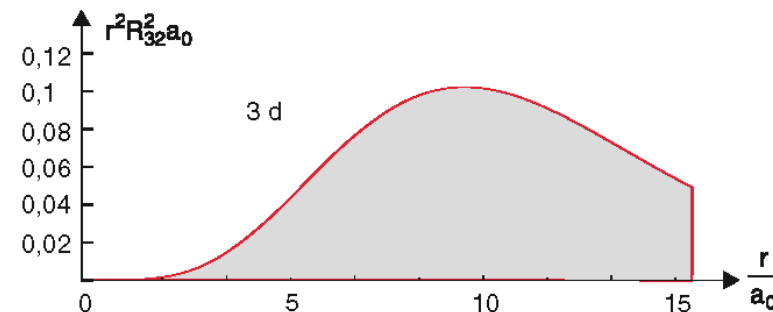
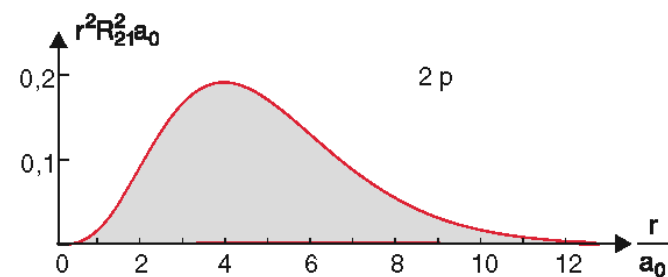
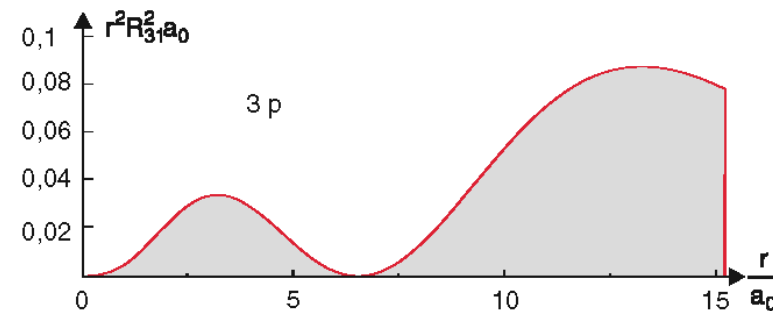
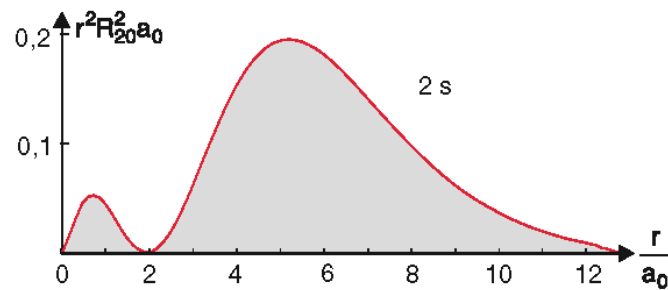
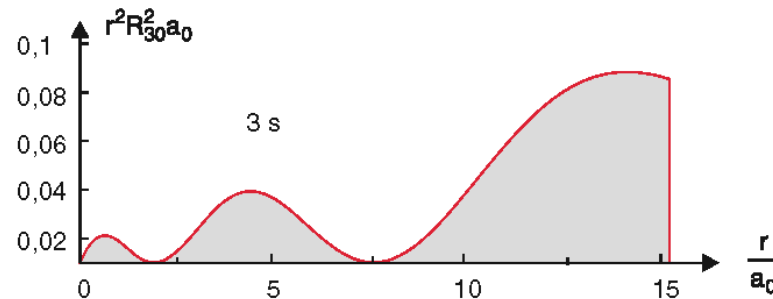
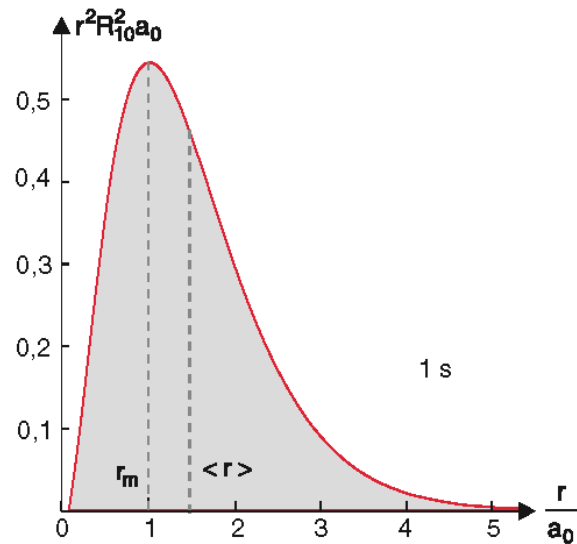
Again: Radial part of the wave function



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

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

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



Some properties

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

$$r_n = n^2 a_B \quad \text{"n-squared times the Bohr radius"}$$

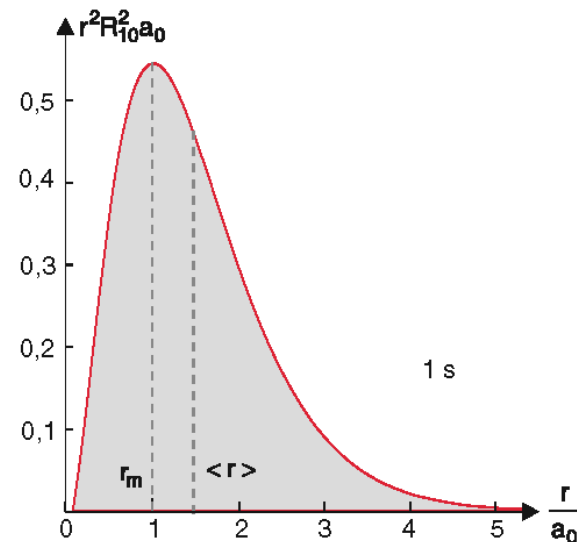
- The **mean distance** is:

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

Example: $n=1$

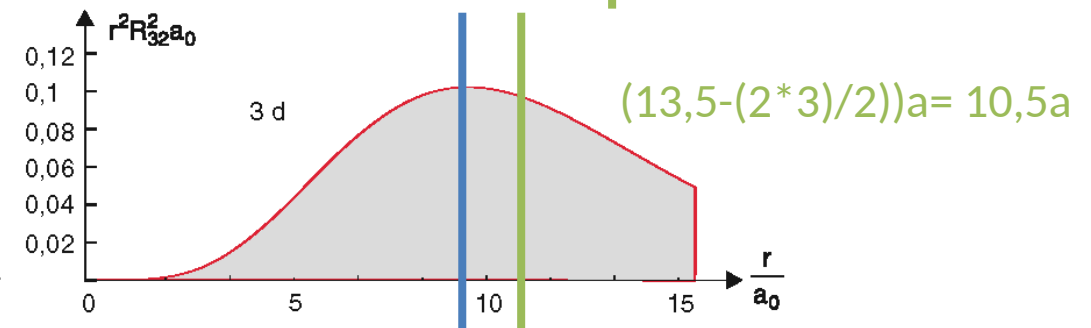
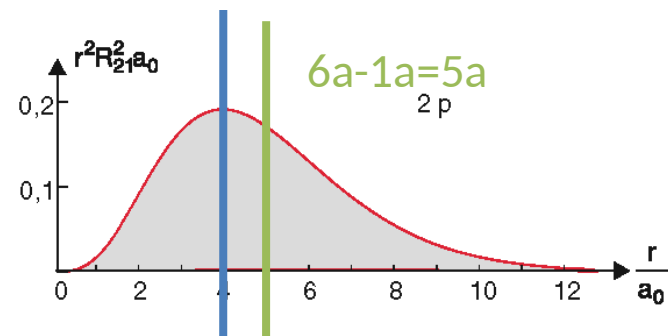
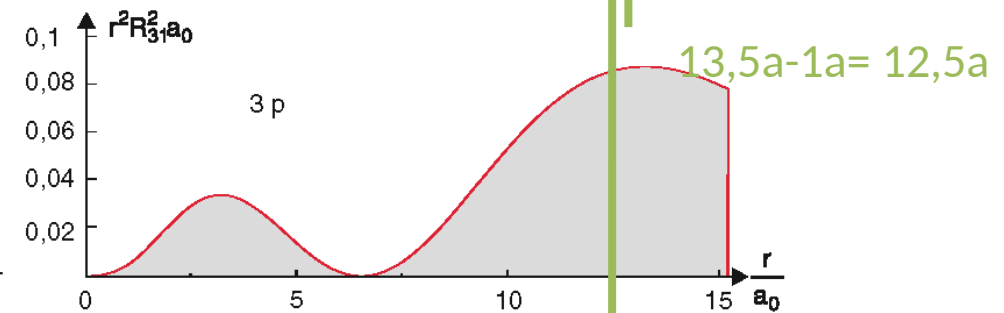
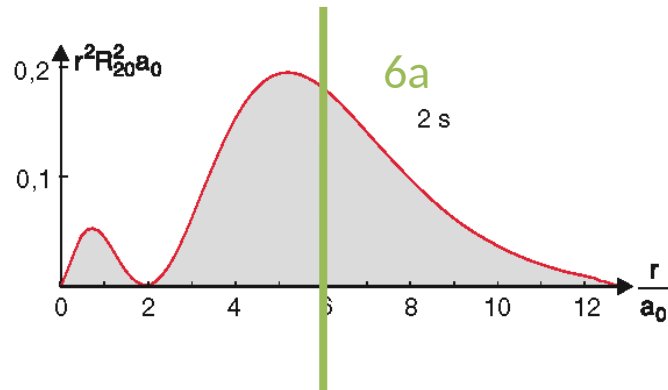
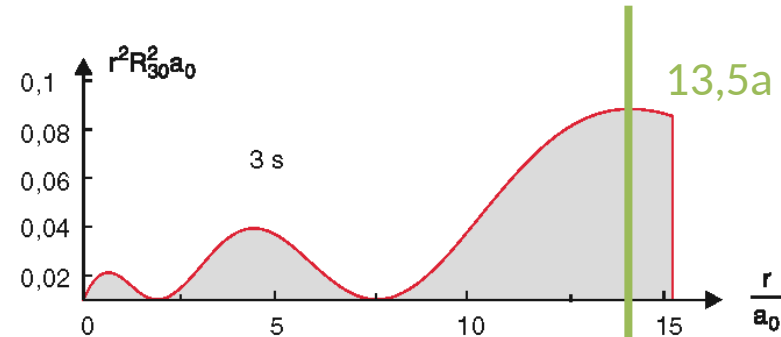
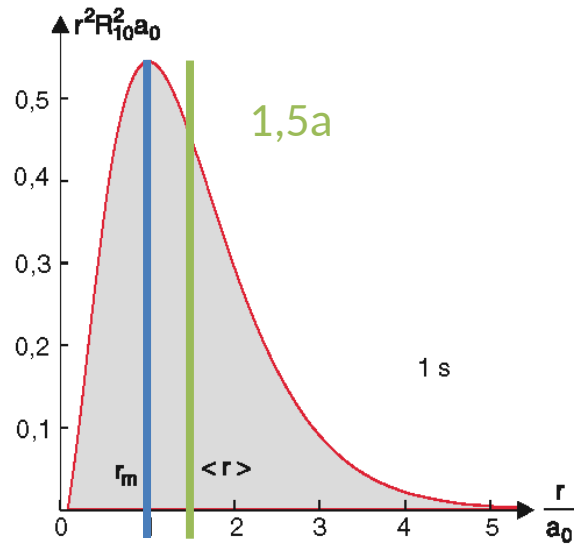
$$r_1 = a_B$$

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



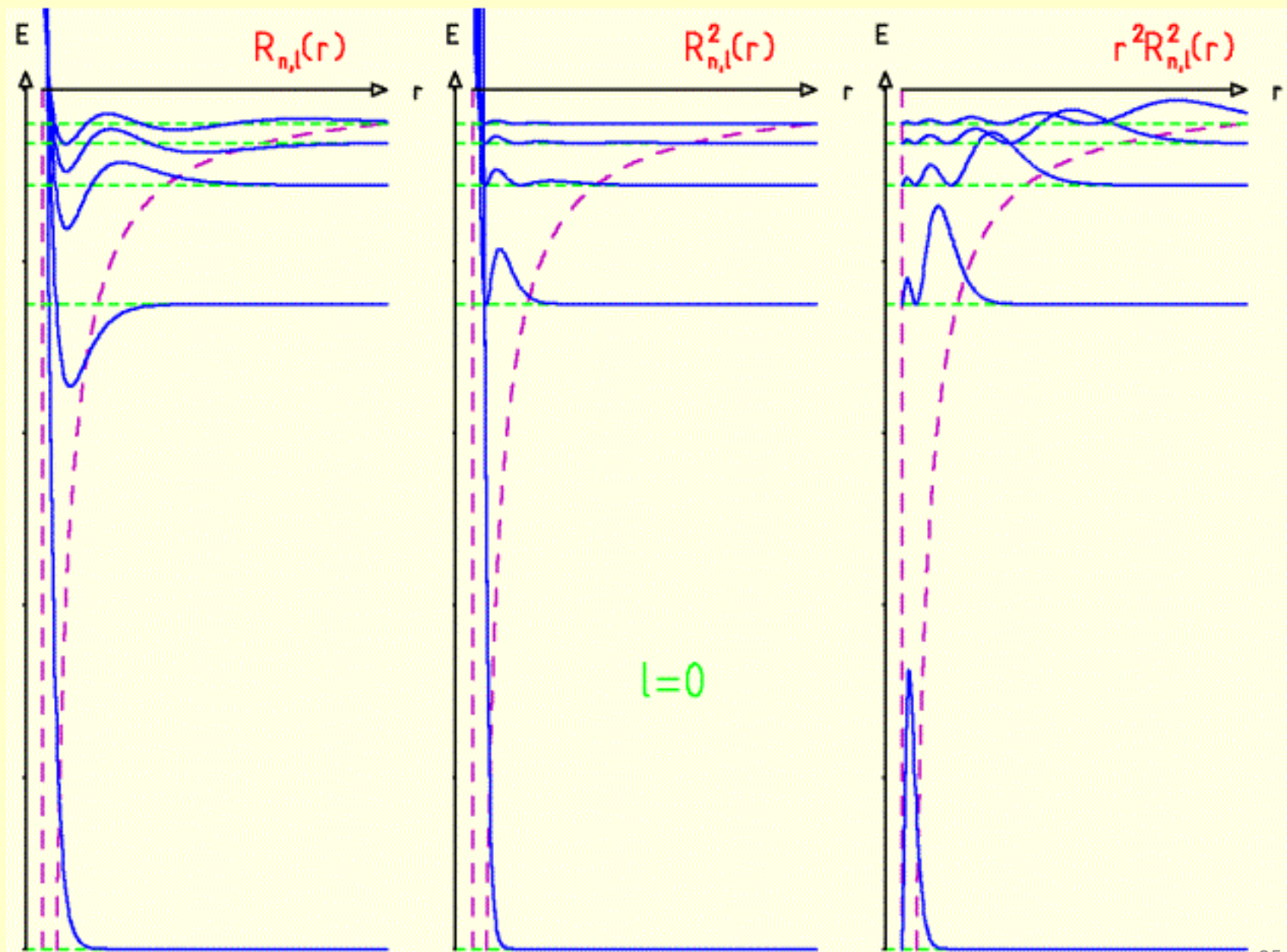
$$r_n = n^2 a_B \quad @l = l_{\max} = n - 1$$

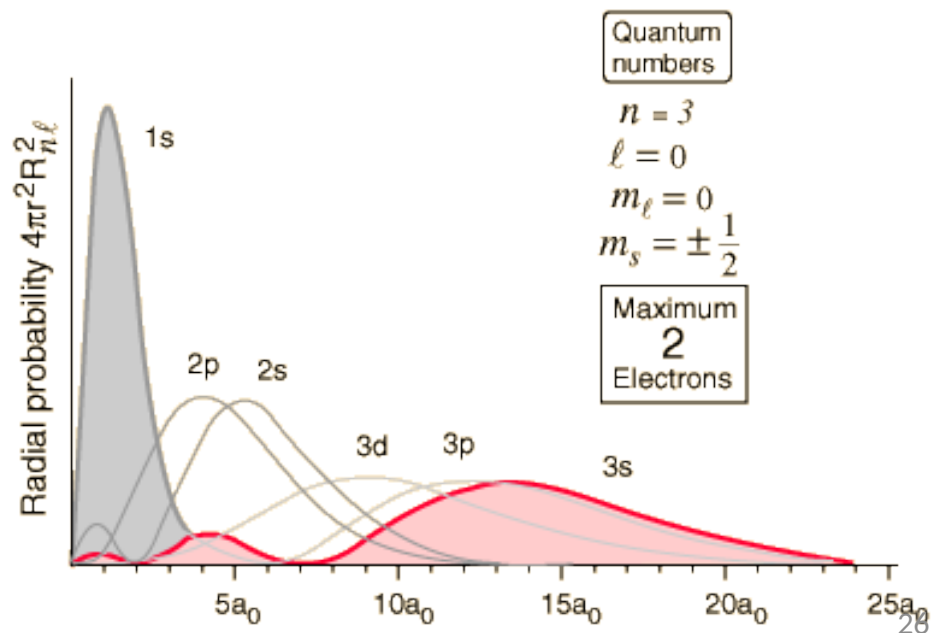
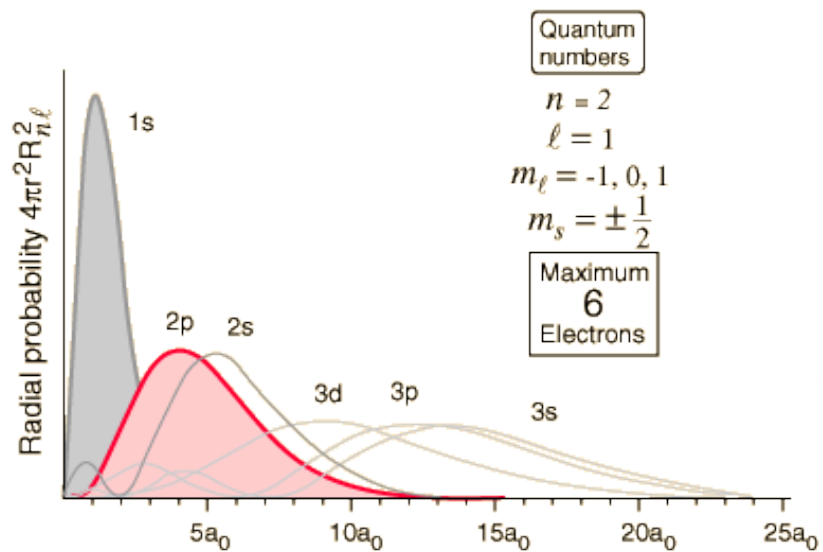
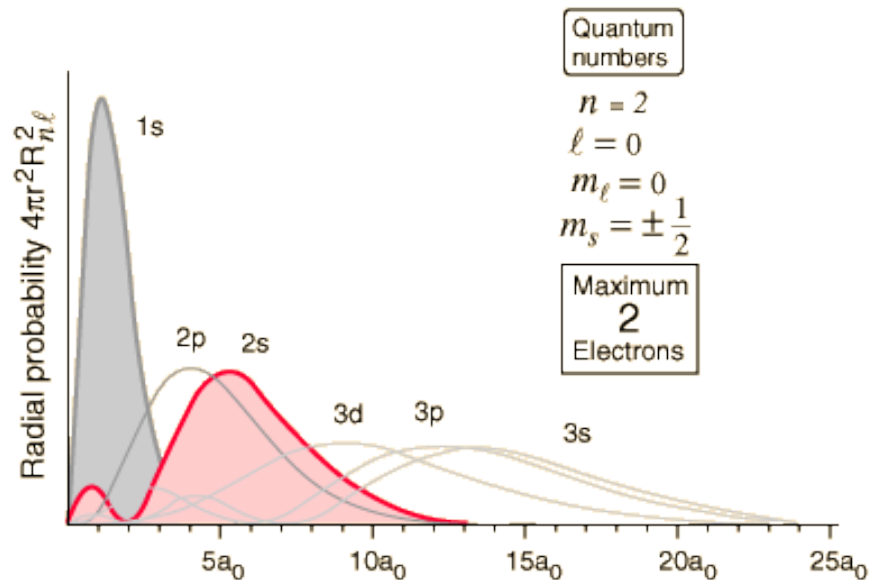
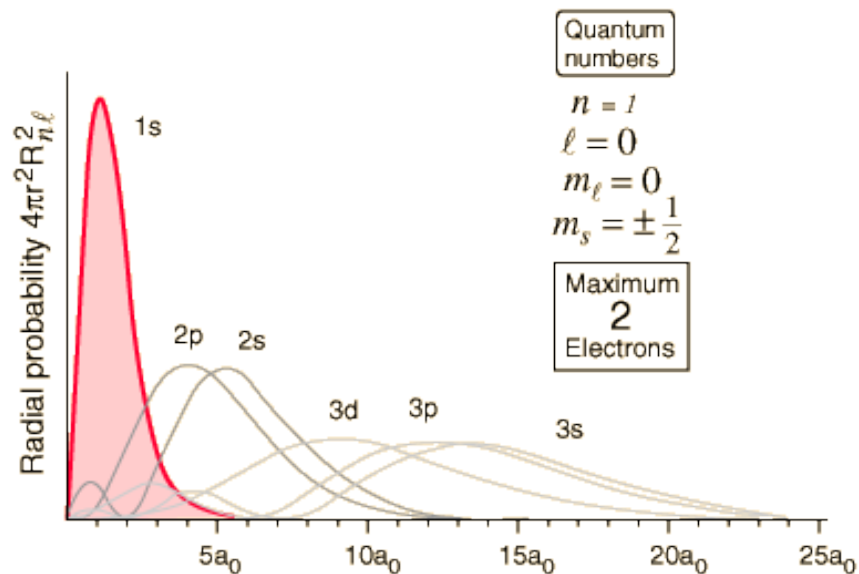
$$\langle r \rangle_{n,l} = a_B \left(\frac{3}{2}n^2 - \frac{l(l+1)}{2} \right)$$



This rough systematic is worth memorizing

Die Eigenzustände des Elektrons im Wasserstoffatom (Radialanteil R)



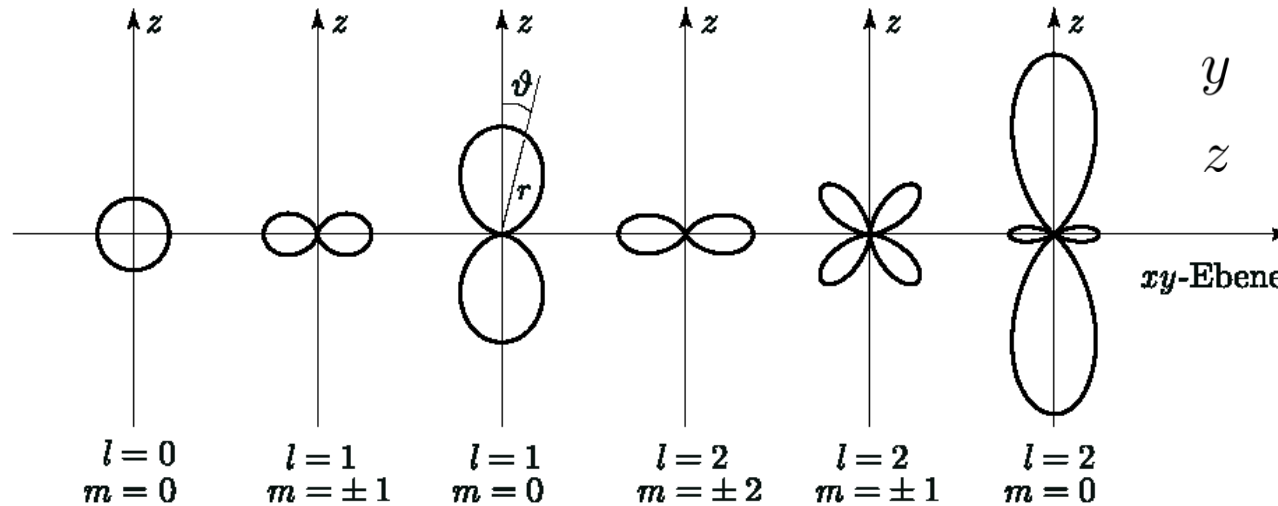


Winkelanteil der Wellenfunktion $Y_{lm}(\theta, \varphi)$

$$x = r \cdot \sin \theta \cos \varphi$$

$$y = r \cdot \sin \theta \sin \varphi$$

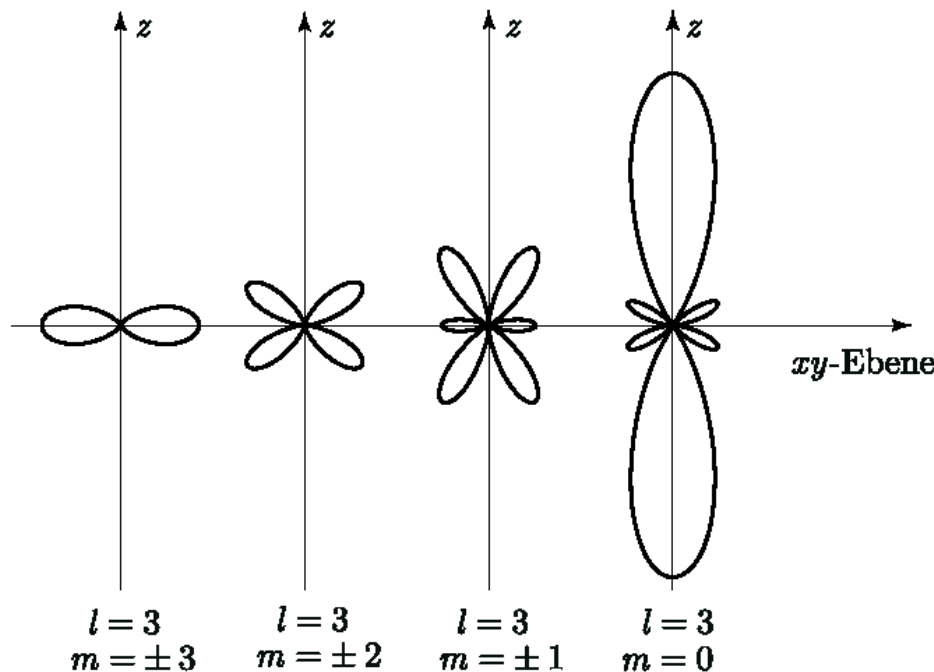
$$z = r \cdot \cos \theta$$



Alles rotations-
symmetrisch um z

d.h. die Länge des Vektors r

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



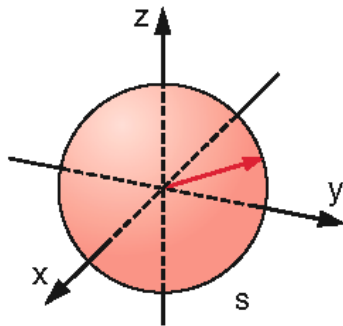
Winkelanteil der Wellenfunktion $Y_{lm}(\theta, \varphi)$

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

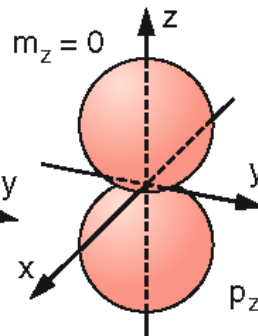
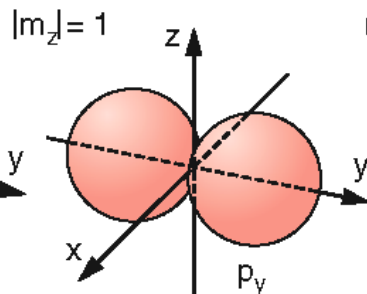
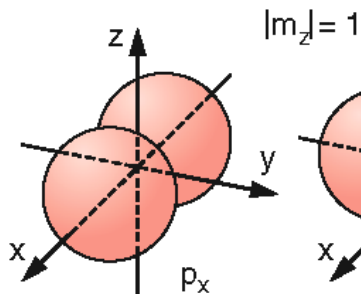
$$Y_{10} = \sqrt{\frac{3}{4\pi}} \cos \theta \quad Y_{11} = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\varphi}$$

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

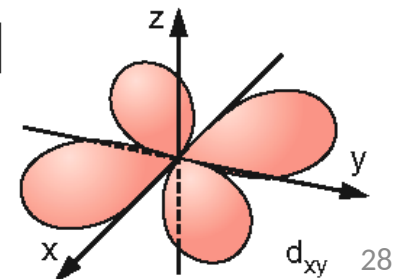
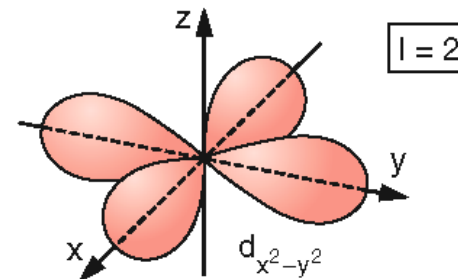
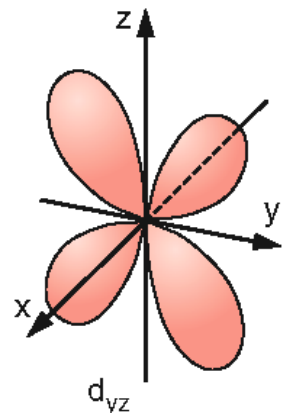
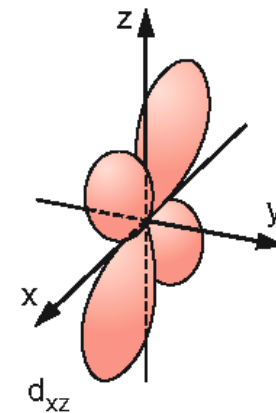
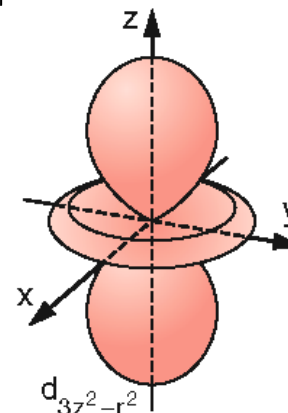
$$|Y_{lm}(x, y, z)|^2$$



$l=0$



$l=1$



$l=2$