Physik III
Atom- und Quantenphysik

Kapitel 7: Das Wasserstoffatom

Prof. Dr. Christian Schönenberger
www.nanoelectronics.ch

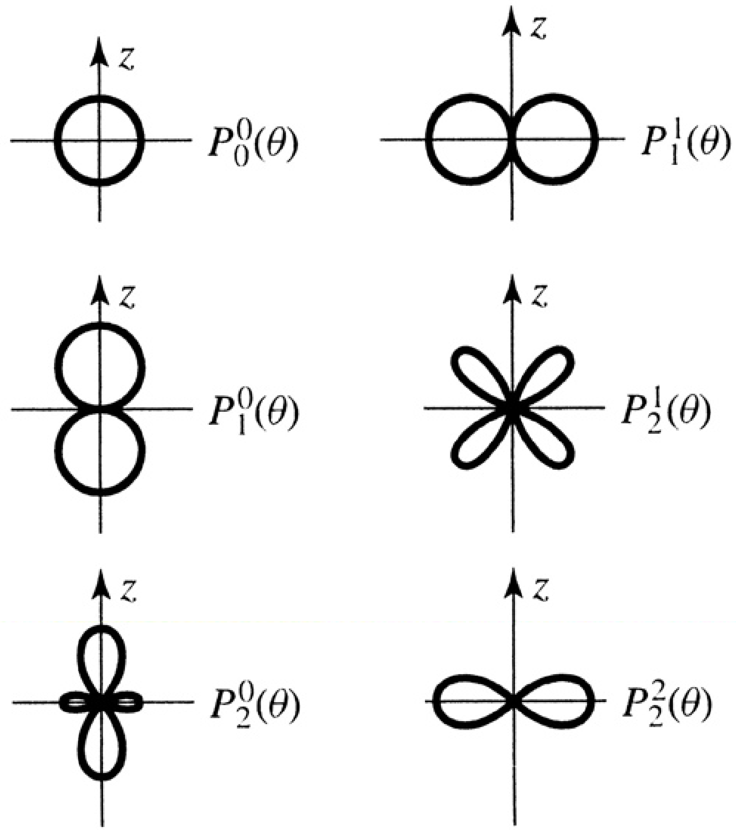
basierend auf der Vorlesung von
Prof. Dr. Philipp Treutlein
http://atom.physik.unibas.ch

zugeordnete Legendrefunktionen

TABLE 4.2: Some associated Legendre functions, $P_l^m(\cos\theta)$: (a) functional form, (b) graphs of $r = P_l^m(\cos\theta)$ (in these plots r tells you the magnitude of the function in the direction θ; each figure should be rotated about the z-axis).

$P_0^0 = 1$	$P_2^0 = \frac{1}{2}(3\cos^2\theta - 1)$
$P_1^1 = \sin\theta$	$P_3^3 = 15\sin\theta(1-\cos^2\theta)$
$P_1^0 = \cos\theta$	$P_3^2 = 15\sin^2\theta\,\cos\theta$
$P_2^2 = 3\sin^2\theta$	$P_3^1 = \frac{3}{2}\sin\theta(5\cos^2\theta - 1)$
$P_2^1 = 3\sin\theta\,\cos\theta$	$P_3^0 = \frac{1}{2}(5\cos^3\theta - 3\cos\theta)$

(a)



(b)

Griffiths, QM

Kugelflächenfunktionen

TABLE 4.3: 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 normalized angular wave functions[8] are called **spherical harmonics**:

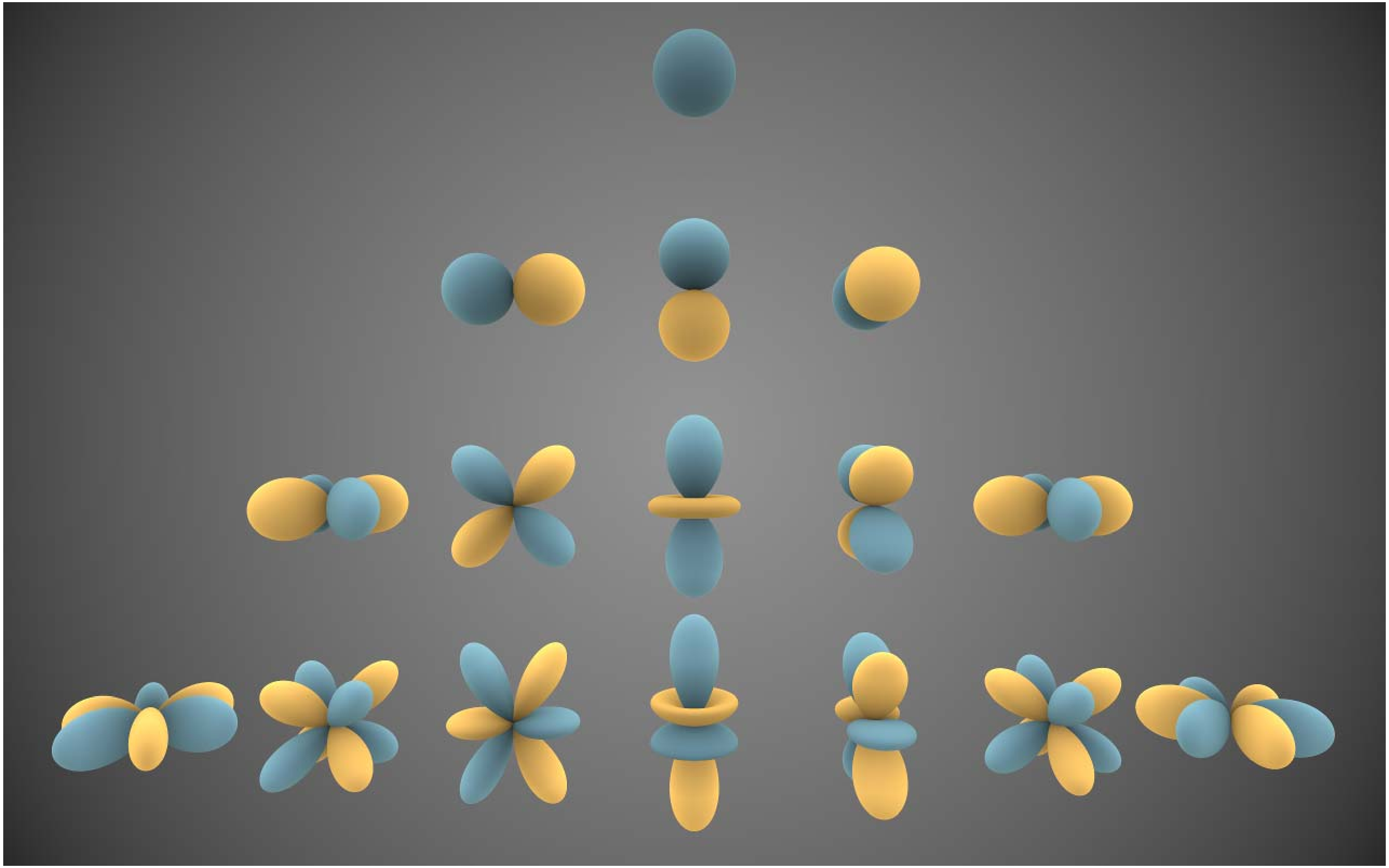
$$Y_l^m(\theta, \phi) = \epsilon\sqrt{\frac{(2l+1)}{4\pi}\frac{(l-|m|)!}{(l+|m|)!}}\, e^{im\phi}\, P_l^m(\cos\theta), \qquad [4.32]$$

where $\epsilon = (-1)^m$ for $m \geq 0$ and $\epsilon = 1$ for $m \leq 0$. As we shall prove later on, they are automatically orthogonal, so

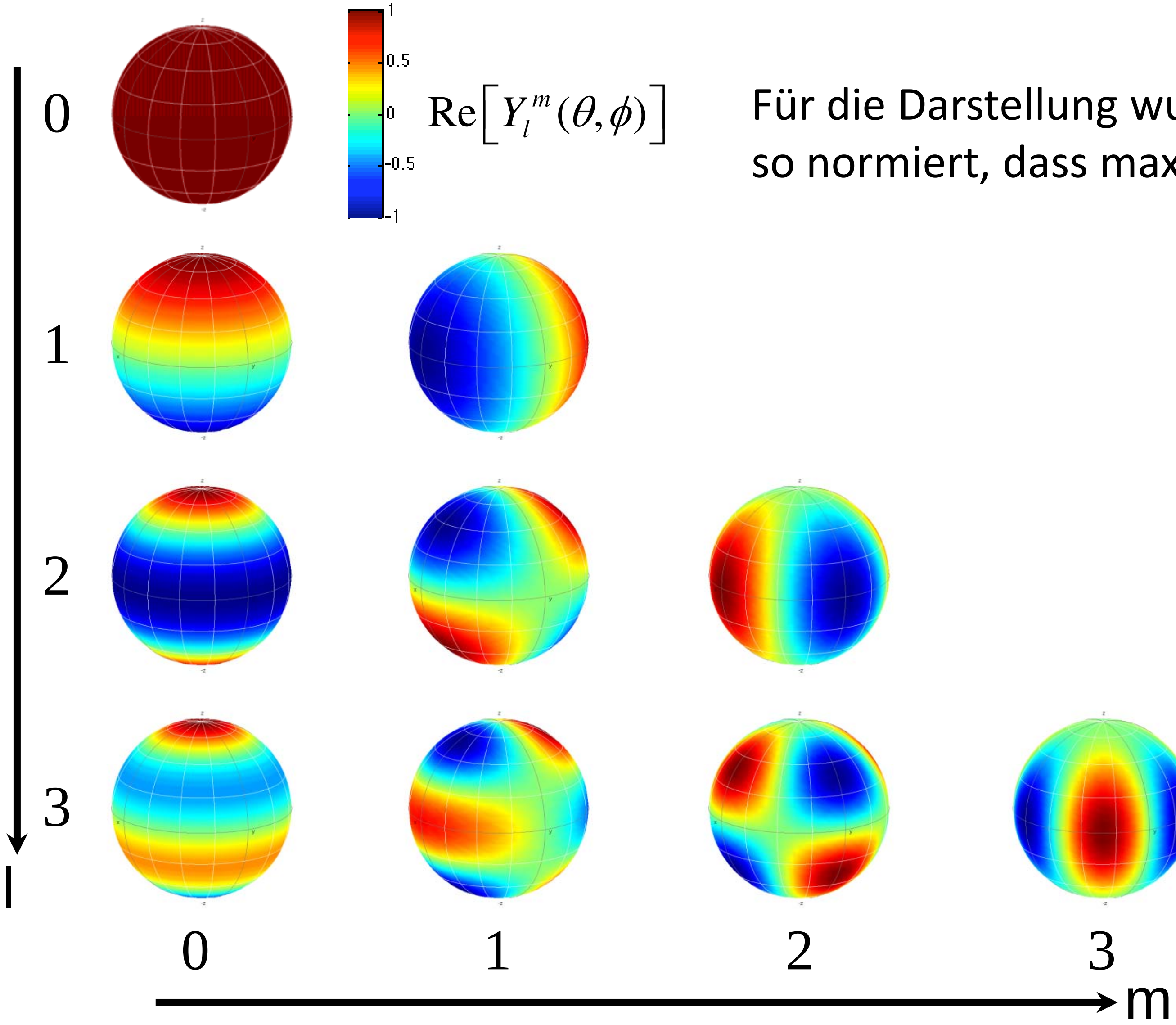
$$\int_0^{2\pi}\int_0^{\pi} [Y_l^m(\theta, \phi)]^*[Y_{l'}^{m'}(\theta, \phi)] \sin\theta\, d\theta\, d\phi = \delta_{ll'}\delta_{mm'}, \qquad [4.33]$$

Griffiths, QM

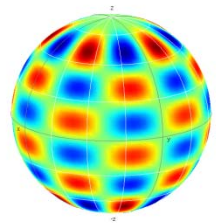
Spherical harmonics



Kugelflächenfunktionen

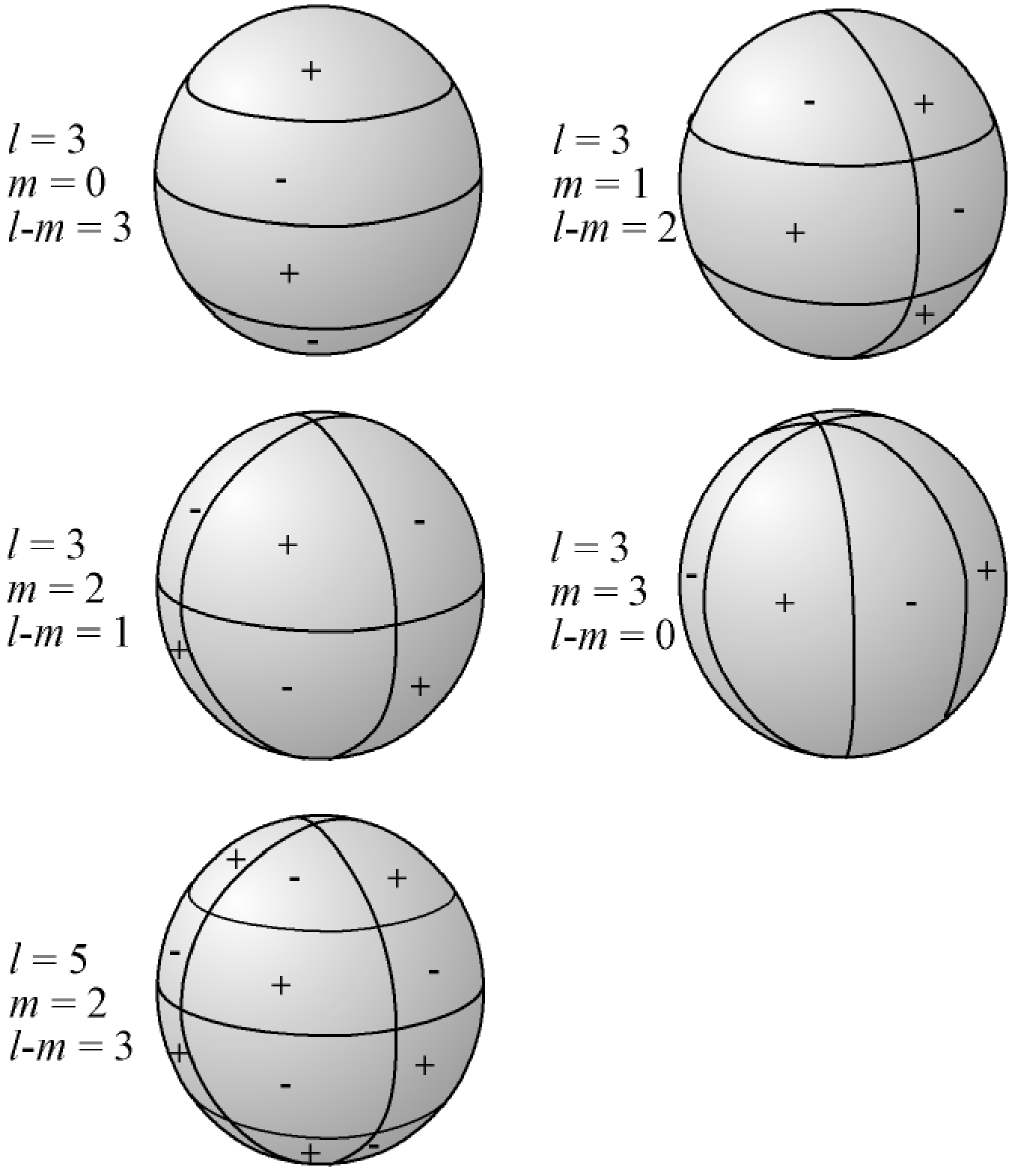


Für die Darstellung wurden die Funktionen so normiert, dass max(Y_l^m) = 1



$\mathrm{Re}\left[Y_{10}^{5}(\theta,\phi)\right]$

Spherical harmonics



Drehimpulsquantisierung

$$\left[\hat{L}_i, \hat{L}_j\right] = i\varepsilon_{ijk}\hat{L}_k$$

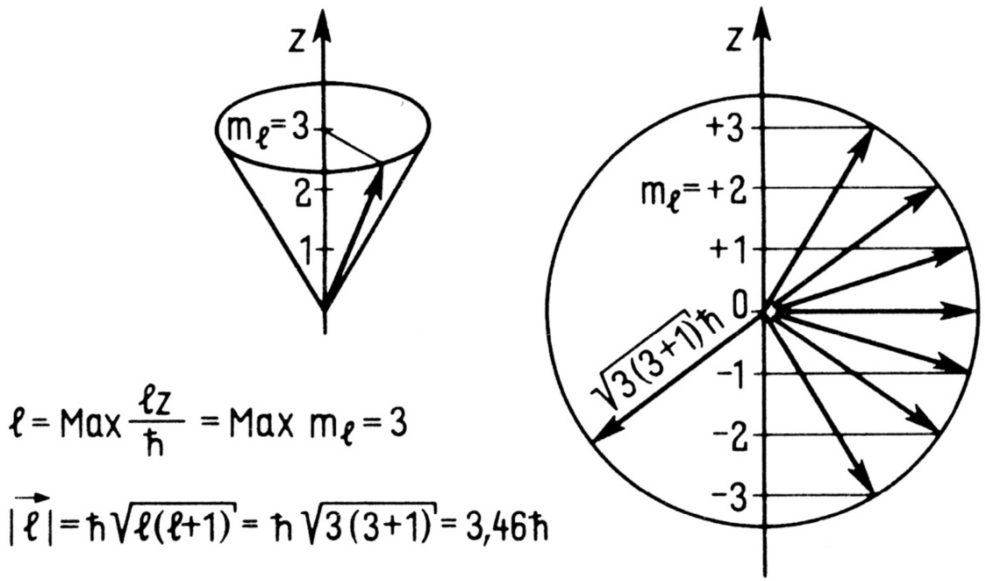
$$\left[\hat{L}^2, \hat{L}_j\right] = 0$$

$$\hat{L}^2 Y_l^m = \hbar^2 l(l+1) Y_l^m \qquad l = 0,1,2\ldots$$

$$\hat{L}_z Y_l^m = \hbar m Y_l^m \quad m = -l, -l+1, \ldots l-1, l$$

Eigenzustand von L_z:
L auf Kegel um z-Achse verschmiert
→ L_x und L_y unscharf, aber L_z scharf

(2l+1) **Einstellmöglichkeiten von L_z**
d.h. erlaubte Werte von m



L_z kann nicht genau in z-Richtung zeigen, da Radius des Kreises grösser als maximaler Betrag von m

Mayer-Kuckuk, Atomphysik, Abb. 31

TABLE 4.5: The first few Laguerre polynomials, $L_q(x)$.

$$L_0 = 1$$

$$L_1 = -x + 1$$

$$L_2 = x^2 - 4x + 2$$

$$L_3 = -x^3 + 9x^2 - 18x + 6$$

$$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$$

$$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$$

$$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$$

Griffiths, QM

TABLE 4.6: Some associated Laguerre polynomials, $L_{q-p}^{p}(x)$.

$L_0^0 = 1$	$L_0^2 = 2$
$L_1^0 = -x + 1$	$L_1^2 = -6x + 18$
$L_2^0 = x^2 - 4x + 2$	$L_2^2 = 12x^2 - 96x + 144$
$L_0^1 = 1$	$L_0^3 = 6$
$L_1^1 = -2x + 4$	$L_1^3 = -24x + 96$
$L_2^1 = 3x^2 - 18x + 18$	$L_2^3 = 60x^2 - 600x + 1200$

Griffiths, QM

Radiale Wellenfunktionen

TABLE 4.7: The first few radial wave functions for hydrogen, $R_{nl}(r)$.

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

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

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

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

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

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

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

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

$$R_{42} = \frac{1}{64\sqrt{5}}a^{-3/2}\left(1-\frac{1}{12}\frac{r}{a}\right)\left(\frac{r}{a}\right)^2\exp(-r/4a)$$

$$R_{43} = \frac{1}{768\sqrt{35}}a^{-3/2}\left(\frac{r}{a}\right)^3\exp(-r/4a)$$

Griffiths, QM

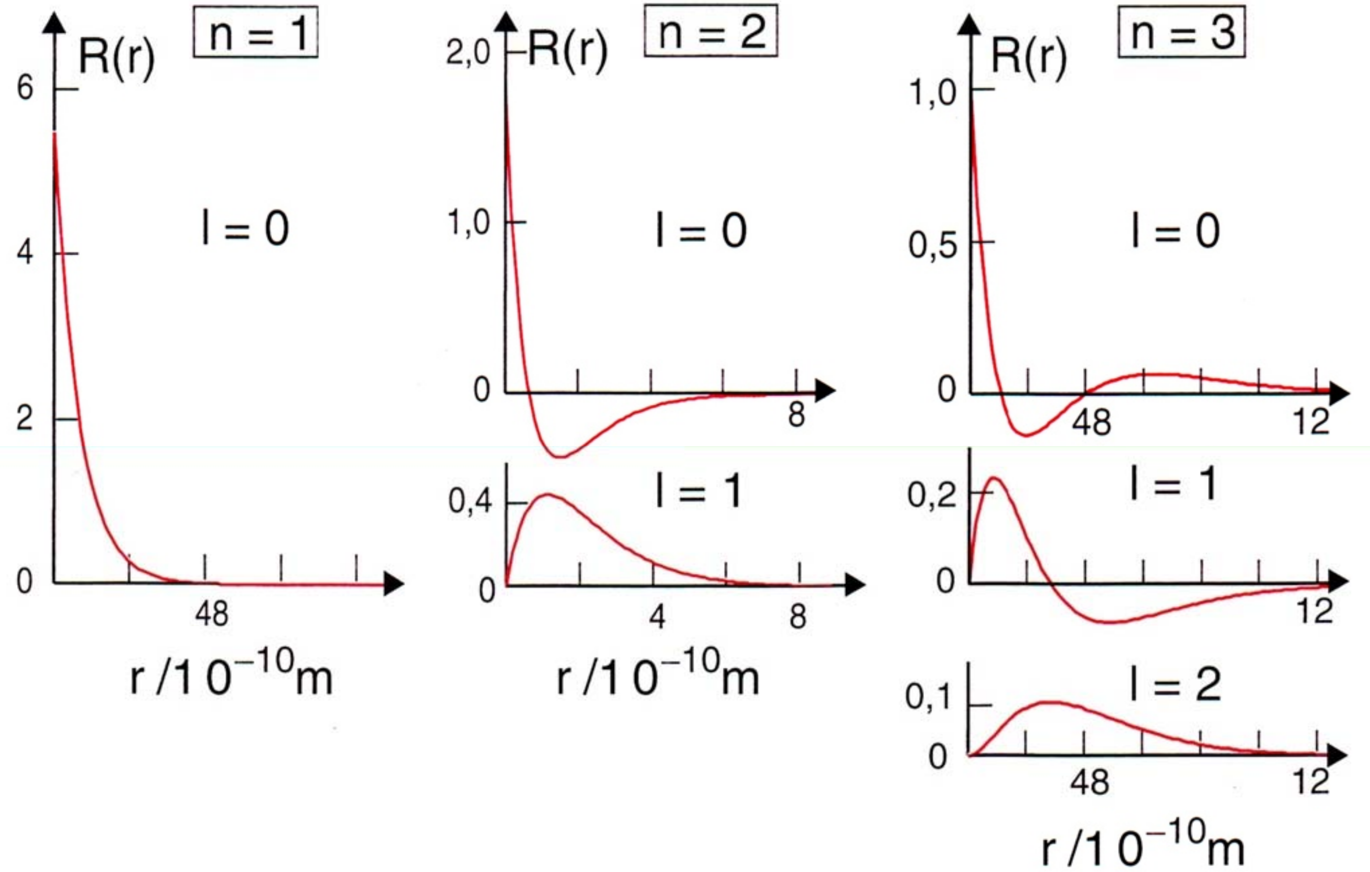


Abb. 5.3. Die Radialfunktionen $R_{n,l}(r)$ des Wasserstoffatoms für die Hauptquantenzahlen $n = 1, 2, 3$. Die Ordinate ist in Einheiten von $10^8\ \text{m}^{-3/2}$ aufgetragen

Demtröder

Vollständige Wellenfkt. H-Atom

$$\psi_{nlm}(r,\theta,\phi) = R_{nl}(r) Y_l^m(\theta,\phi)$$

$$\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na)\right] Y_l^m(\theta,\phi).$$

Quantenzahlen:

n = 1, 2, 3, ...	Hauptquantenzahl
l = 0, 1, 2, ... , n-1	Drehimpulsquantenzahl
m = -l, ... , l	magnetische Quantenzahl

Bohrscher Radius:

$$a_0 = \frac{4\pi\varepsilon_0 h^2}{m_e e^2} = 0.529$$

Vollständige Wellenfkt. H-Atom

Tabelle 5.2. Die normierten vollständigen Eigenfunktionen eines Elektrons im Coulombpotential $V(r) = -Z \cdot e^2/(4\pi\varepsilon_0 r)$

n	l	m	Eigenfunktionen $\psi_{n,l,m}(r,\vartheta,\varphi)$	
1	0	0	$\frac{1}{\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2} e^{-Zr/a_0}$	s-Orbital in 1. Schale
2	0	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(2-\frac{Zr}{a_0}\right) e^{-Zr/2a_0}$	s-Orbital in 2. Schale
2	1	0	$\frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\cos\vartheta$	3 p-Orbitale in 2. Schale
2	1	±1	$\frac{1}{8\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Zr}{a_0} e^{-Zr/2a_0}\sin\vartheta\, e^{\pm i\varphi}$	
3	0	0	$\frac{1}{81\sqrt{3\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(27-18\frac{Zr}{a_0}+2\frac{Z^2r^2}{a_0^2}\right) e^{-Zr/3a_0}$	s-Orbital in 3. Schale
3	1	0	$\frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\cos\vartheta$	3 p-Orbitale in 3. Schale
3	1	±1	$\frac{1}{81}\sqrt{\frac{2}{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\left(6-\frac{Zr}{a_0}\right)\frac{Zr}{a_0} e^{-Zr/3a_0}\sin\vartheta\, e^{\pm i\varphi}$	
3	2	0	$\frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}(3\cos^2\vartheta-1)$	5 d-Orbitale in 3. Schale
3	2	±1	$\frac{1}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin\vartheta\cos\vartheta\, e^{\pm i\varphi}$	
3	2	±2	$\frac{1}{162\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{3/2}\frac{Z^2r^2}{a_0^2} e^{-Zr/3a_0}\sin^2\vartheta\, e^{\pm 2i\varphi}$	

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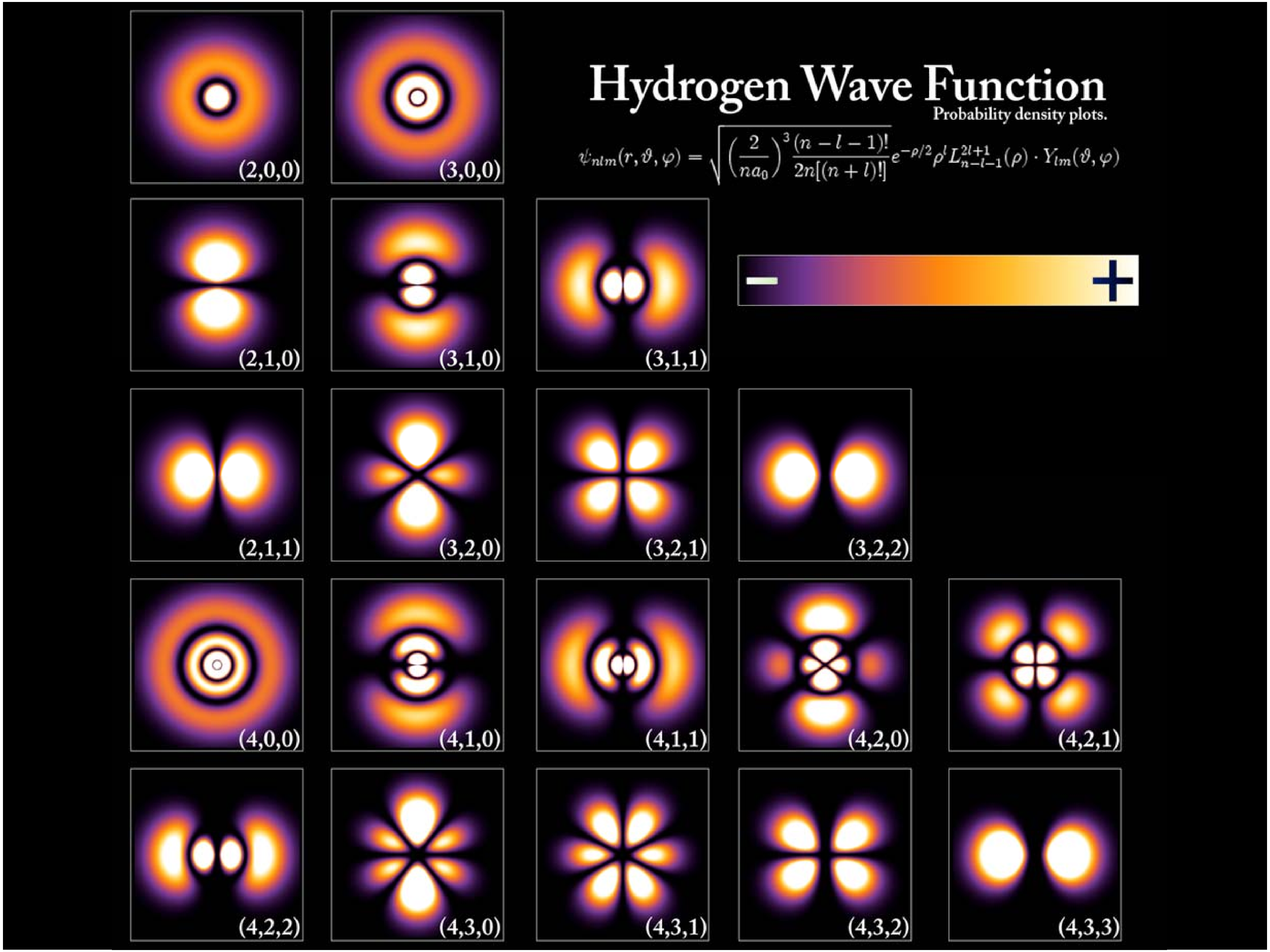

Hydrogen Wave Function
Probability density plots.
$\psi_{nlm}(r,\vartheta,\varphi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]}} e^{-\rho/2} \rho^l L^{2l+1}_{n-l-1}(\rho) \cdot Y_{lm}(\vartheta,\varphi)$
−
+
(2,0,0)
(3,0,0)
(2,1,0)
(3,1,0)
(3,1,1)
(2,1,1)
(3,2,0)
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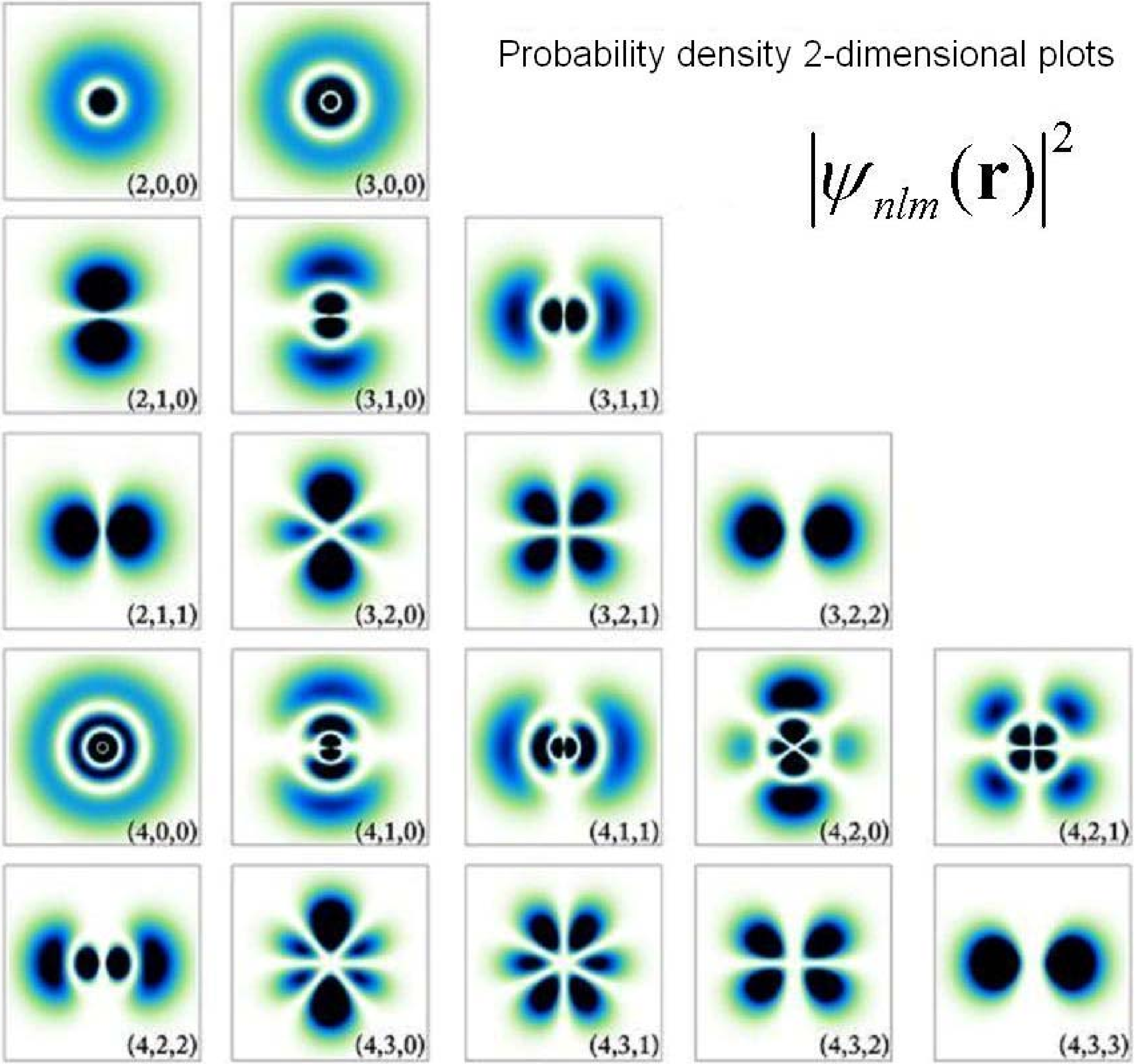
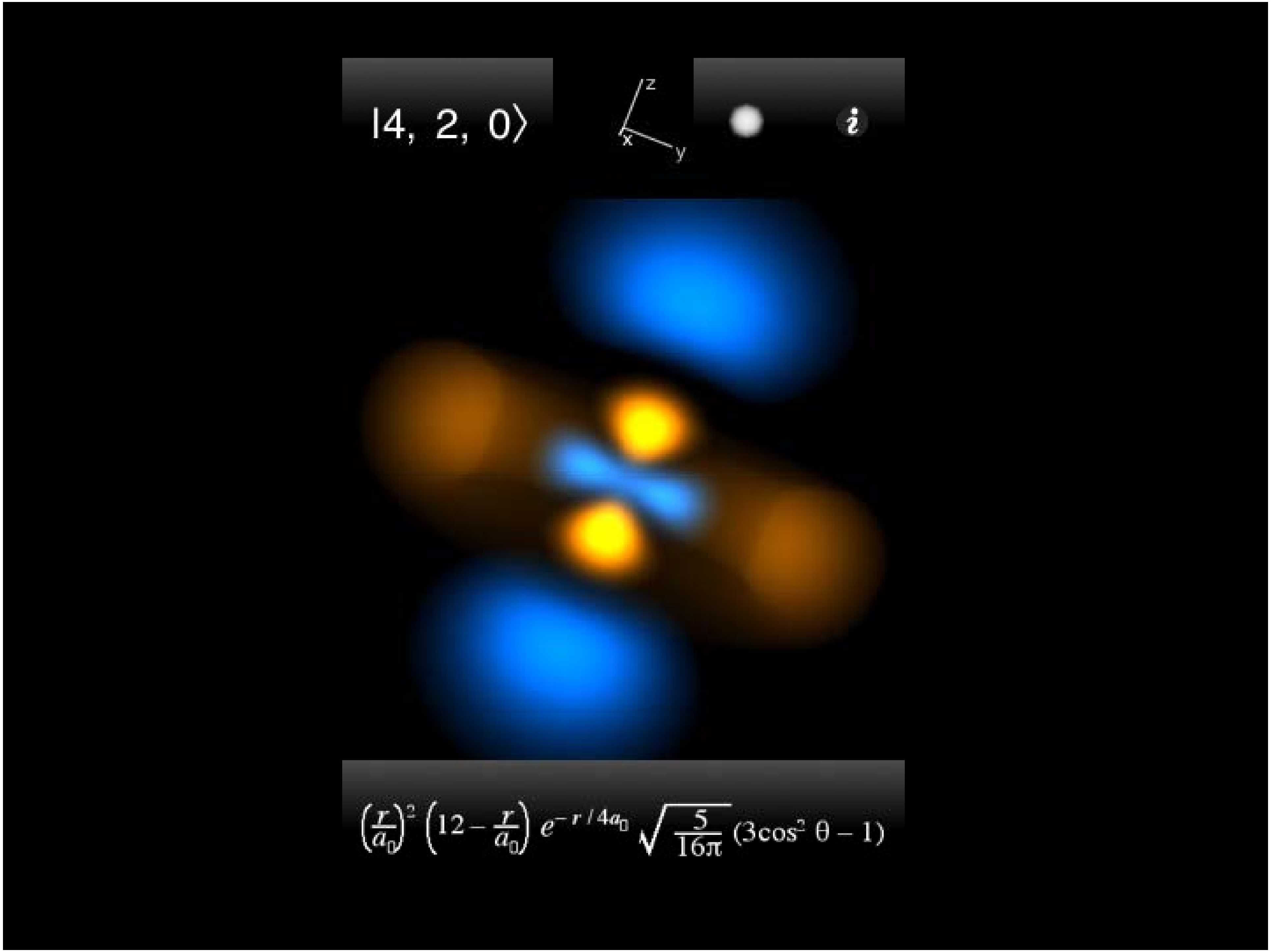
(4,2,1)
(4,2,2)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)

Probability density 2-dimensional plots

$$\left|\psi_{nlm}(\mathbf{r})\right|^2$$




|4, 2, 0⟩
z
x
y
i
$\left(\frac{r}{a_0}\right)^2 \left(12 - \frac{r}{a_0}\right) e^{-r/4a_0} \sqrt{\frac{5}{16\pi}} (3\cos^2\theta - 1)$

Atomare Orbitale

	s (*l*=0)	*p* (*l*=1)			*d* (*l*=2)					*f* (*l*=3)						
	m=0	m=0	m=±1		m=0	m=±1		m=±2		m=0	m=±1		m=±2		m=±3	
	s	p_z	p_x	p_y	d_{z^2}	d_{xz}	d_{yz}	d_{xy}	$d_{x^2-y^2}$	f_{z^3}	f_{xz^2}	f_{yz^2}	f_{xyz}	$f_{z(x^2-y^2)}$	$f_{x(x^2-3y^2)}$	$f_{y(3x^2-y^2)}$
n=1																
n=2																
n=3																
n=4																
n=5										...	...	...	...	...	...	...
n=6					...	...	...	...	...	...	...	...	...	...	...	...
n=7		...	...	...	...	...	...	...	...	...	...	...	...	...	...	...

Orbitalbezeichnung

What do the letters s, p, d, and f in the orbital names stand for?

You might expect that the 's' stands for 'spherical' and 'p' stands for 'polar' because these imply the shapes of the *s* and *p* orbitals, but unfortunately, the letter designations have nothing to do with the orbital shapes.

Spectroscopists associated transitions involving energy levels with different ℓ values with different groups of lines in the line spectra of the alkali metals. The line groups were called *sharp*, *principal*, *diffuse*, and *fundamental*. When the angular momentum quantum number was used to describe and explain these groups of lines, *s* became an abbreviation for $\ell = 0$, *p* meant $\ell = 1$, *d* meant $\ell = 2$, and *f* meant $\ell = 3$. For consistency, higher values of the angular momentum quantum numbers are designated alphabetically (*g* means $\ell = 4$, *h* means $\ell = 5$, and so on).

Author: Fred Senese senese@antoine.frostburg.edu

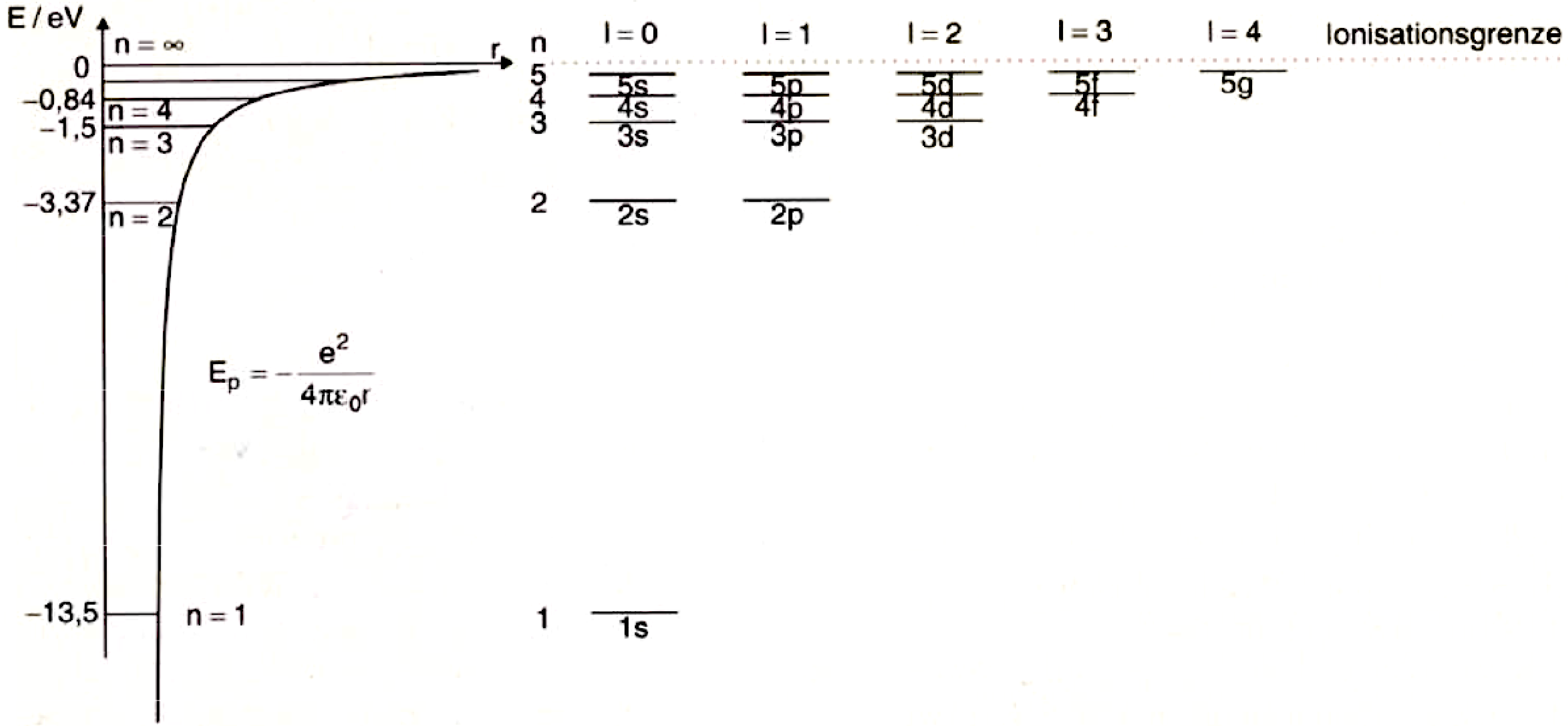
A brief introduction to the history behind these labels can be found in W. B. Jensen, "The origin of the s, p, d, f orbital labels," J. Chem. Educ., vol. 84, no. 5, pp. 757-758, May 2007. [Online]. Available: http://dx.doi.org/10.1021/ed084p757 Apparently the "sharp," "principal," and "diffuse" characterizations were devised first by the British chemists George Liveing and Sir James Dewar in the 1870s (their papers were compiled and published as Collected papers on spectroscopy, which is available online at http://catalog.hathitrust.org/Re...), and the "fundamental" characterization came later, due to the work of Arno Bergmann around 1907.

Energieniveaus H-Atom

$$E = \frac{E_1}{n^2}, \quad n = 1, 2, 3, \ldots \qquad E_1 = -\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\varepsilon_0}\right)^2$$ =-13.6 eV

Grundzustands-
/Ionisationsenergie

Jedes Energieniveau ist n^2-fach entartet, da E nicht von l und m abhängt.



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