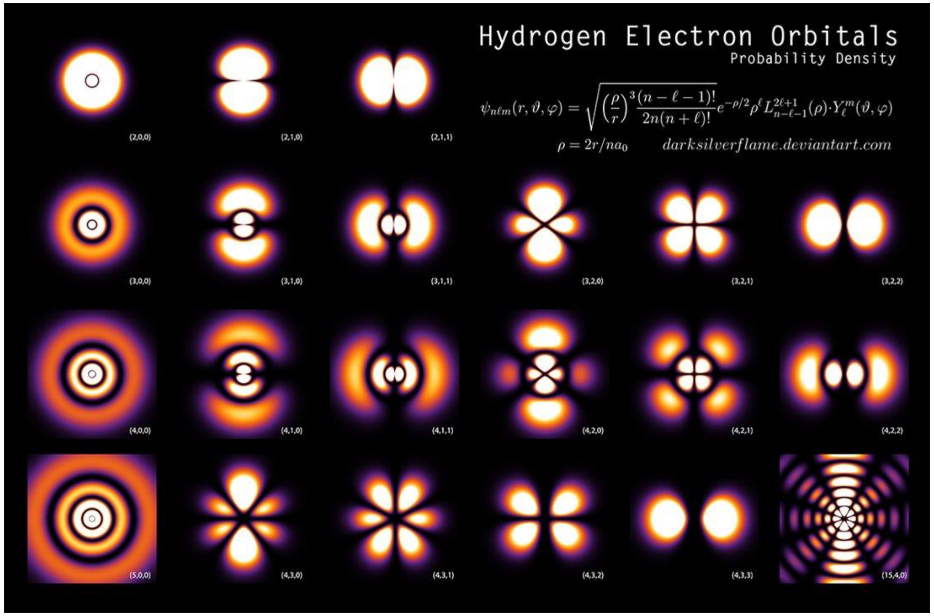
Quantum Physics 1

Key formulas and extra pictures
on the
quantum description of the hydrogen atom



The main idea in Sec. 4.1 and 4.2 is to characterize/describe the quantum states of the hydrogen atom

This means, that it is nothing more or less than working out

$$\hat{H}\left|\Psi_i\right\rangle = E_i\left|\Psi_i\right\rangle$$

This is now a problem in 3D, it is solved in spherical coordinates, and then it looks like

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2\psi}{\partial\phi^2}\right)\right] + V\psi = E\psi. \qquad [4.14]$$

where $V = V(r) = \frac{-1}{4\pi\varepsilon_0}\frac{|e|^2}{r}$ [4.52]

and it leads to a bit more algebra than for a particle in a 1D infinitely deep potential well…..

But the final results can be fully summarized by 3 integer quantum numbers
(defining the eigen values) *n*, *l*, and *m*,
and is much more concise and elegant than the pages of algebra that lead to this result.

In 3D, a particle that moves around a nucleus has angular momentum. First a question about this:

What is the character of the set of eigenvalues for an operator for angular momentum (and what is the reason, give the best answer)?

A) Continuous: It is like the position of a free particle, it can take on any value when measured.
B) Continuous: Since there are no boundary conditions for the eigenvalue problem.
C) Discrete: Since you only get discrete answers when you measure it.
D) Discrete: Since the eigenstates need to fulfill constructive interference with themselves upon rotation.

Periodic boundary conditions for the eigenvalue problem.

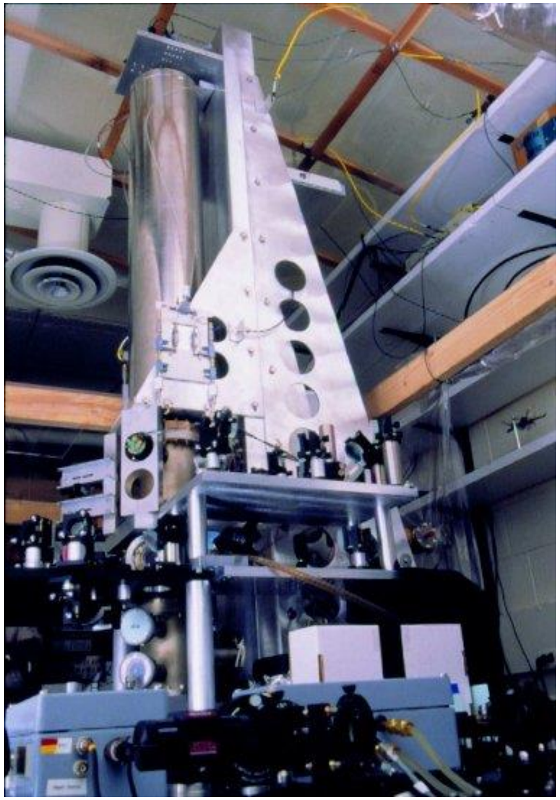
Done on the black board:
Tutorial and discussion on how to build an atomic clock

These weeks also: re-visit the postulates of week 2, now in Dirac notation.

Atomic clocks

1991 Cesium standard clock

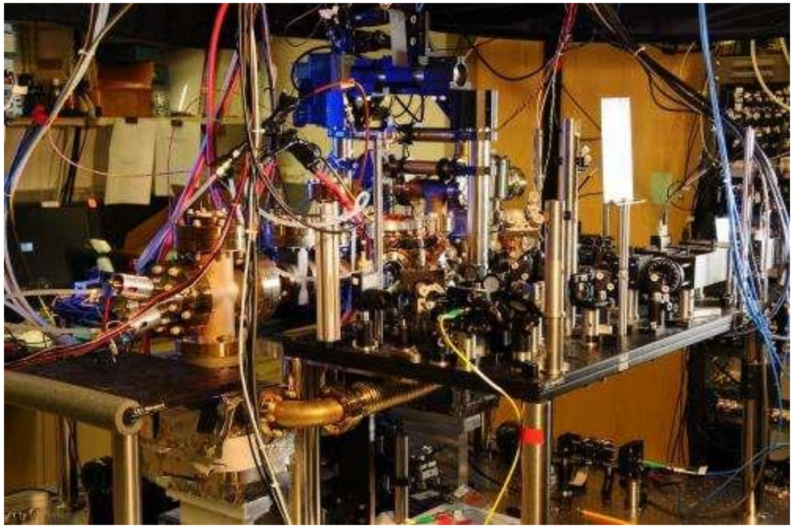
NIST-F1 begins operation with an uncertainty of 1.7×10^{-15}, or accuracy to about one second in 20 million years.
Crucial for GPS and many other applications.



Source: http://tf.nist.gov/cesium/atomichistory.htm

2013 New research

NIST ytterbium atomic clocks set record for stability.
Ticks stable to within less than two parts in 10^{18}.



Source: http://phys.org/news/2013-08-nist-ytterbium-atomic-clocks-stability.html

Some key point in the derivation as in the Griffiths book, p. 136

$$\Theta(\theta) = A P_l^m(\cos\theta), \quad [4.26]$$

where P_l^m is the **associated Legendre function**, defined by[6]

$$P_l^m(x) \equiv (1 - x^2)^{|m|/2} \left(\frac{d}{dx}\right)^{|m|} P_l(x). \quad [4.27]$$

and $P_l(x)$ is the lth **Legendre polynomial**, defined by the **Rodrigues formula**:

$$P_l(x) \equiv \frac{1}{2^l l!} \left(\frac{d}{dx}\right)^l (x^2 - 1)^l. \quad [4.28]$$

TABLE 4.1: The first few Legendre polynomials, $P_l(x)$: (a) functional form, (b) graphs.

$$P_0 = 1$$

$$P_1 = x$$

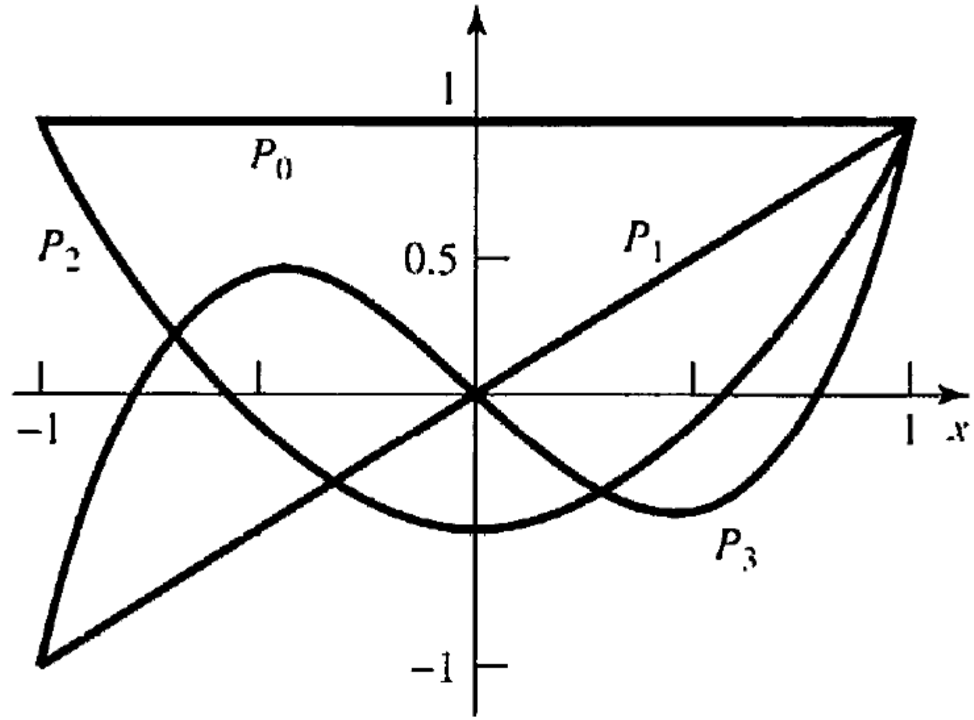
$$P_2 = \frac{1}{2}(3x^2 - 1)$$

$$P_3 = \frac{1}{2}(5x^3 - 3x)$$

$$P_4 = \frac{1}{8}(35x^4 - 30x^2 + 3)$$

$$P_5 = \frac{1}{8}(63x^5 - 70x^3 + 15x)$$

(a)

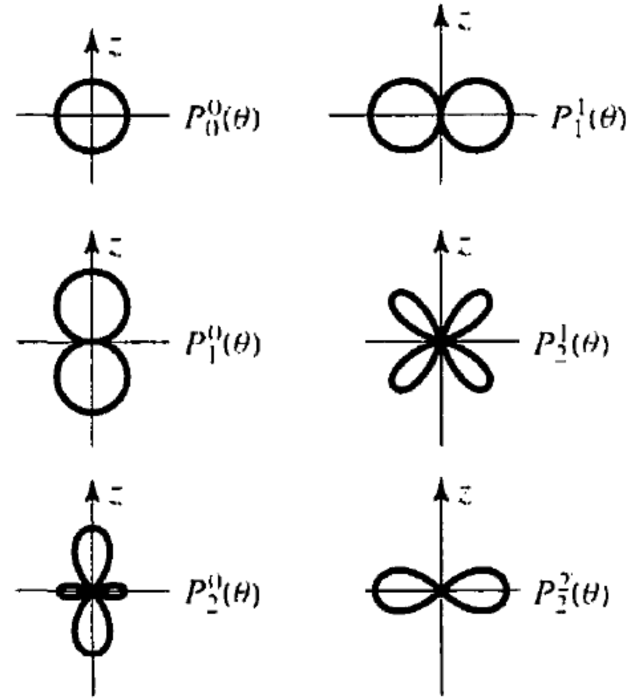


(b)

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)

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**:

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

TABLE 4.4: The first few spherical Bessel and Neumann functions, $j_n(x)$ and $n_l(x)$; asymptotic forms for small x.

$j_0 = \frac{\sin x}{x}$	$n_0 = -\frac{\cos x}{x}$
$j_1 = \frac{\sin x}{x^2} - \frac{\cos x}{x}$	$n_1 = -\frac{\cos x}{x^2} - \frac{\sin x}{x}$
$j_2 = \left(\frac{3}{x^3} - \frac{1}{x}\right)\sin x - \frac{3}{x^2}\cos x$	$n_2 = -\left(\frac{3}{x^3} - \frac{1}{x}\right)\cos x - \frac{3}{x^2}\sin x$
$j_l \rightarrow \frac{2^l l!}{(2l+1)!}x^l,$	$n_l \rightarrow -\frac{(2l)!}{2^l l!}\frac{1}{x^{l+1}}$, for $x \ll 1$.

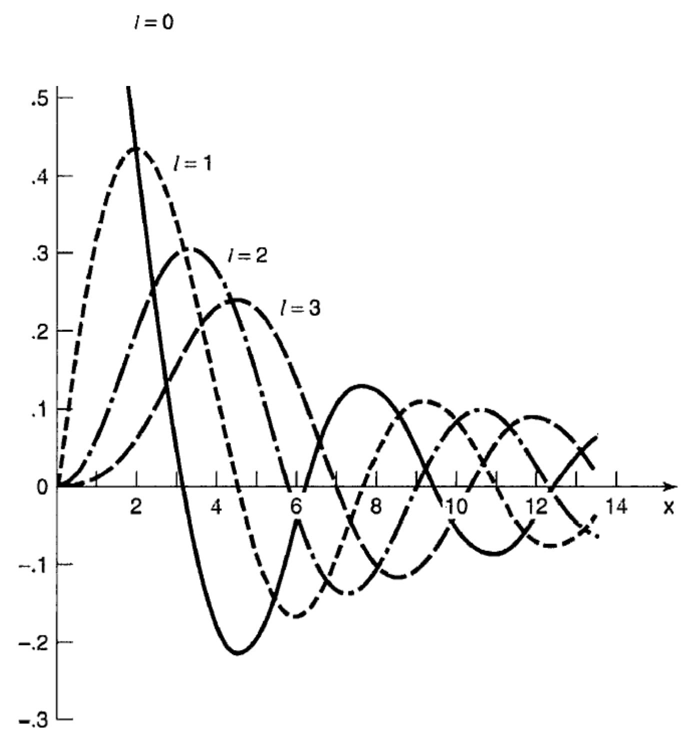


FIGURE 4.2: Graphs of the first four spherical Bessel functions.

where

$$L_{q-p}^{p}(x) \equiv (-1)^p \left(\frac{d}{dx}\right)^p L_q(x) \qquad [4.87]$$

is an **associated Laguerre polynomial**, and

$$L_q(x) \equiv e^x \left(\frac{d}{dx}\right)^q \left(e^{-x}x^q\right) \qquad [4.88]$$

is the qth **Laguerre polynomial.**[16] (The first few Laguerre polynomials are listed in Table 4.5; some associated Laguerre polynomials are given in Table 4.6. The first few radial wave functions are listed in Table 4.7, and plotted in Figure 4.4.) The normalized hydrogen wave functions are[17]

$$\boxed{\psi_{nlm} = \sqrt{\left(\frac{2}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}}\, e^{-r/na} \left(\frac{2r}{na}\right)^l \left[L_{n-l-1}^{2l+1}(2r/na)\right] Y_l^m(\theta, \phi).} \qquad [4.89]$$

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

$L_0 = 1$
$L_1 = -x + 1$
$L_2 = x^2 - 4x + 2$
$L_3 = -x^3 + 9x^2 - 18x + 6$
$L_4 = x^4 - 16x^3 + 72x^2 - 96x + 24$
$L_5 = -x^5 + 25x^4 - 200x^3 + 600x^2 - 600x + 120$
$L_6 = x^6 - 36x^5 + 450x^4 - 2400x^3 + 5400x^2 - 4320x + 720$

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

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

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

$R_{10} = 2a^{-3/2}\exp(-r/a)$
$R_{20} = \frac{1}{\sqrt{2}}a^{-3/2}\left(1-\frac{1}{2}\frac{r}{a}\right)\exp(-r/2a)$
$R_{21} = \frac{1}{\sqrt{24}}a^{-3/2}\frac{r}{a}\exp(-r/2a)$
$R_{30} = \frac{2}{\sqrt{27}}a^{-3/2}\left(1-\frac{2}{3}\frac{r}{a}+\frac{2}{27}\left(\frac{r}{a}\right)^2\right)\exp(-r/3a)$
$R_{31} = \frac{8}{27\sqrt{6}}a^{-3/2}\left(1-\frac{1}{6}\frac{r}{a}\right)\left(\frac{r}{a}\right)\exp(-r/3a)$
$R_{32} = \frac{4}{81\sqrt{30}}a^{-3/2}\left(\frac{r}{a}\right)^2\exp(-r/3a)$
$R_{40} = \frac{1}{4}a^{-3/2}\left(1-\frac{3}{4}\frac{r}{a}+\frac{1}{8}\left(\frac{r}{a}\right)^2-\frac{1}{192}\left(\frac{r}{a}\right)^3\right)\exp(-r/4a)$
$R_{41} = \frac{\sqrt{5}}{16\sqrt{3}}a^{-3/2}\left(1-\frac{1}{4}\frac{r}{a}+\frac{1}{80}\left(\frac{r}{a}\right)^2\right)\frac{r}{a}\exp(-r/4a)$
$R_{42} = \frac{1}{64\sqrt{5}}a^{-3/2}\left(1-\frac{1}{12}\frac{r}{a}\right)\left(\frac{r}{a}\right)^2\exp(-r/4a)$
$R_{43} = \frac{1}{768\sqrt{35}}a^{-3/2}\left(\frac{r}{a}\right)^3\exp(-r/4a)$

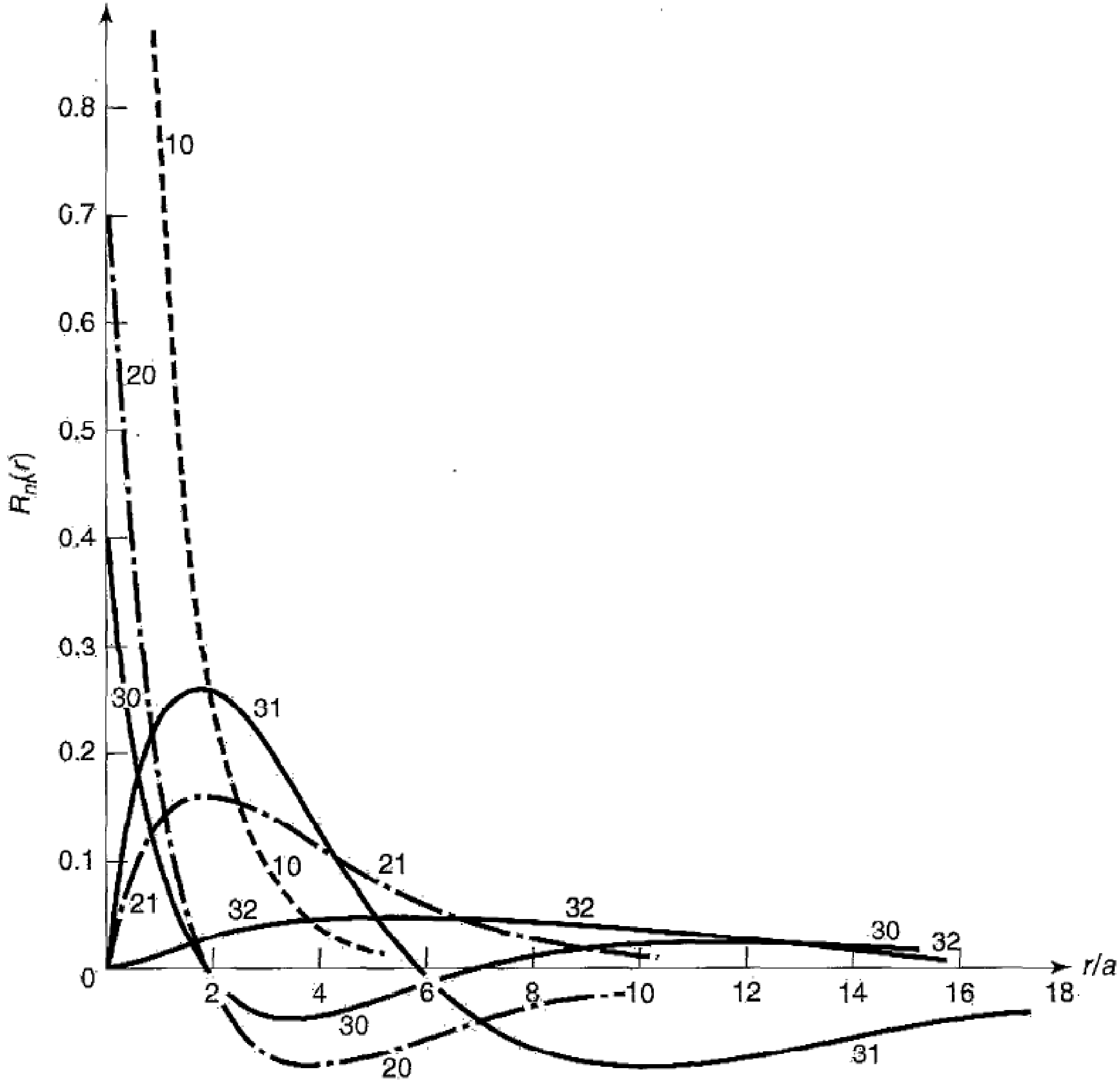


FIGURE 4.4: Graphs of the first few hydrogen radial wave functions, $R_{nl}(r)$.

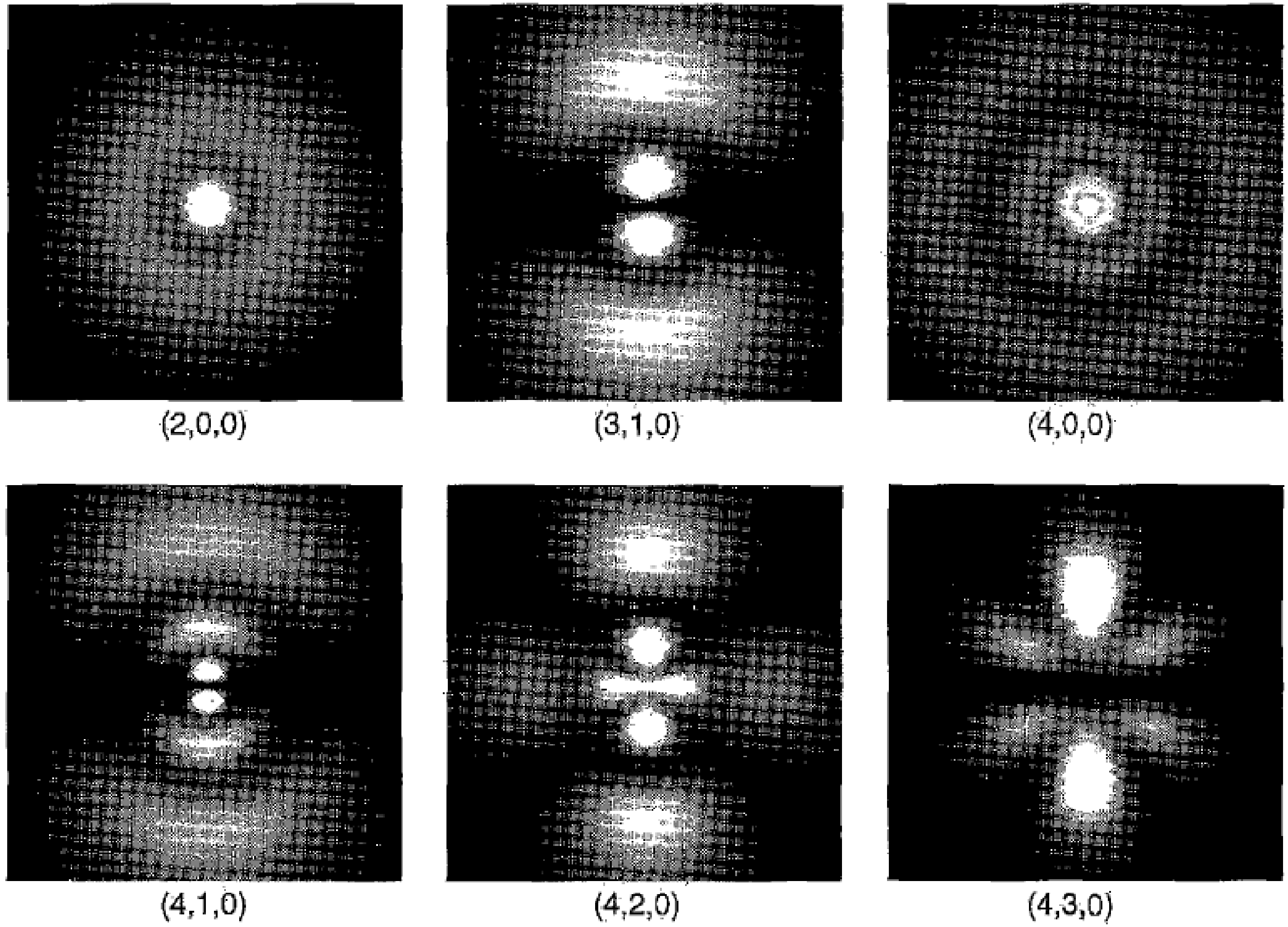
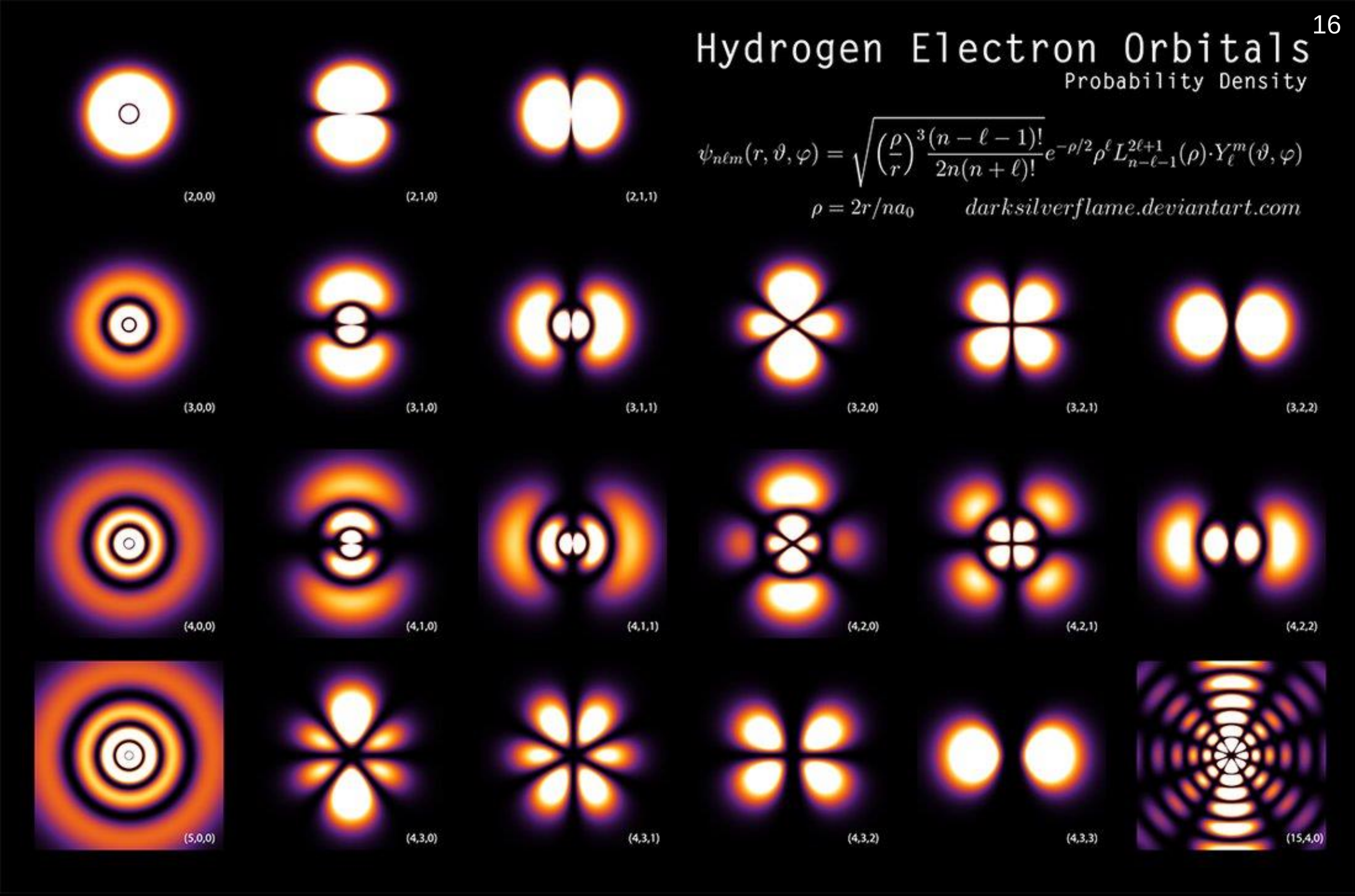


FIGURE 4.5: Density plots for the hydrogen wave functions (n, l, m). Imagine each plot to be rotated about the (vertical) z axis. Printed by permission using "Atom in a Box," v1.0.8, by Dauger Research. You can make your own plots by going to the Web site http://dauger.com.


Hydrogen Electron Orbitals
Probability Density
$\psi_{n\ell m}(r,\vartheta,\varphi) = \sqrt{\left(\frac{\rho}{r}\right)^3 \frac{(n-\ell-1)!}{2n(n+\ell)!}} e^{-\rho/2} \rho^\ell L_{n-\ell-1}^{2\ell+1}(\rho) \cdot Y_\ell^m(\vartheta,\varphi)$
$\rho = 2r/na_0$
darksilverflame.deviantart.com
(2,0,0)
(2,1,0)
(2,1,1)
(3,0,0)
(3,1,0)
(3,1,1)
(3,2,0)
(3,2,1)
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(5,0,0)
(4,3,0)
(4,3,1)
(4,3,2)
(4,3,3)
(15,4,0)

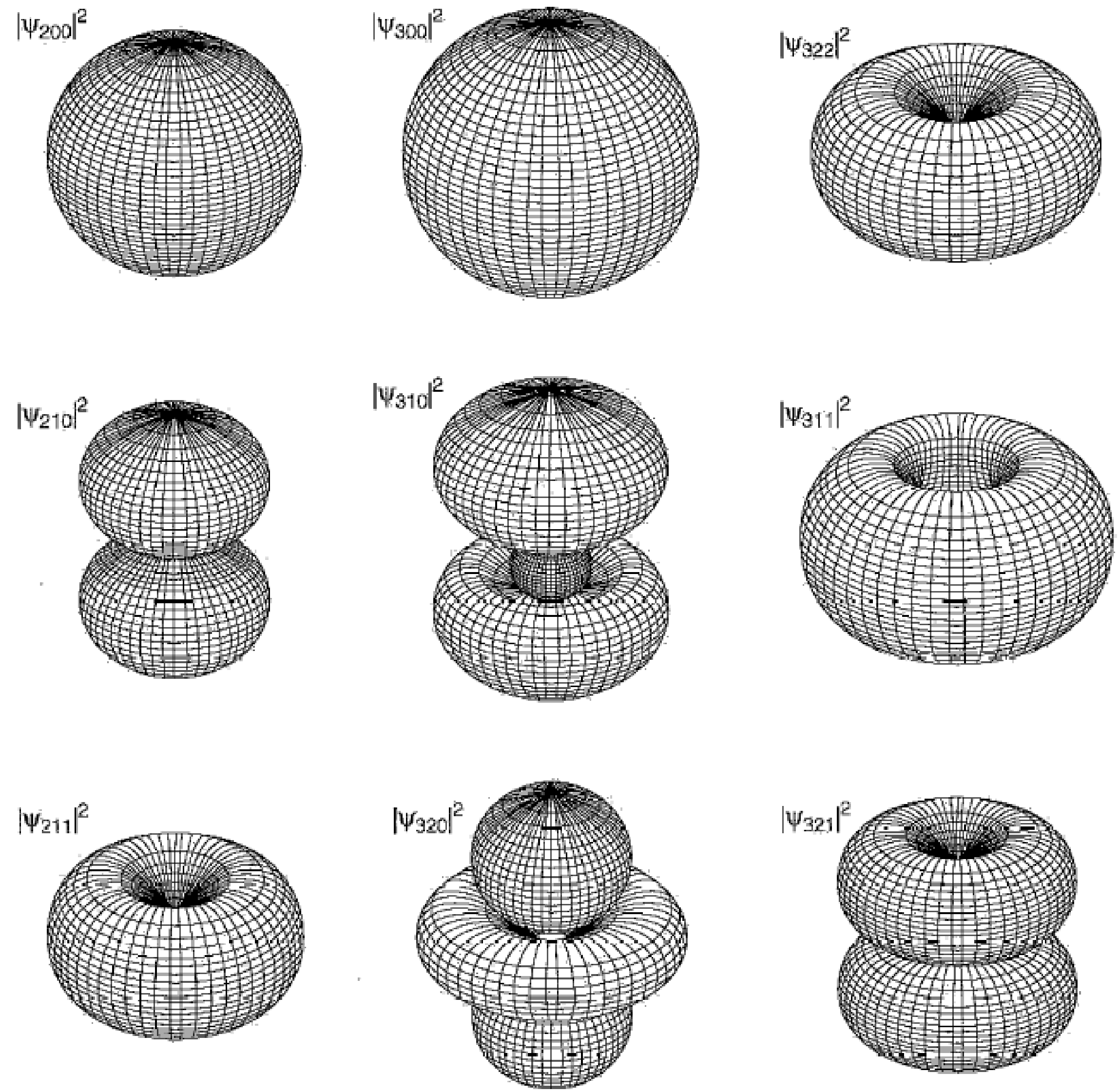
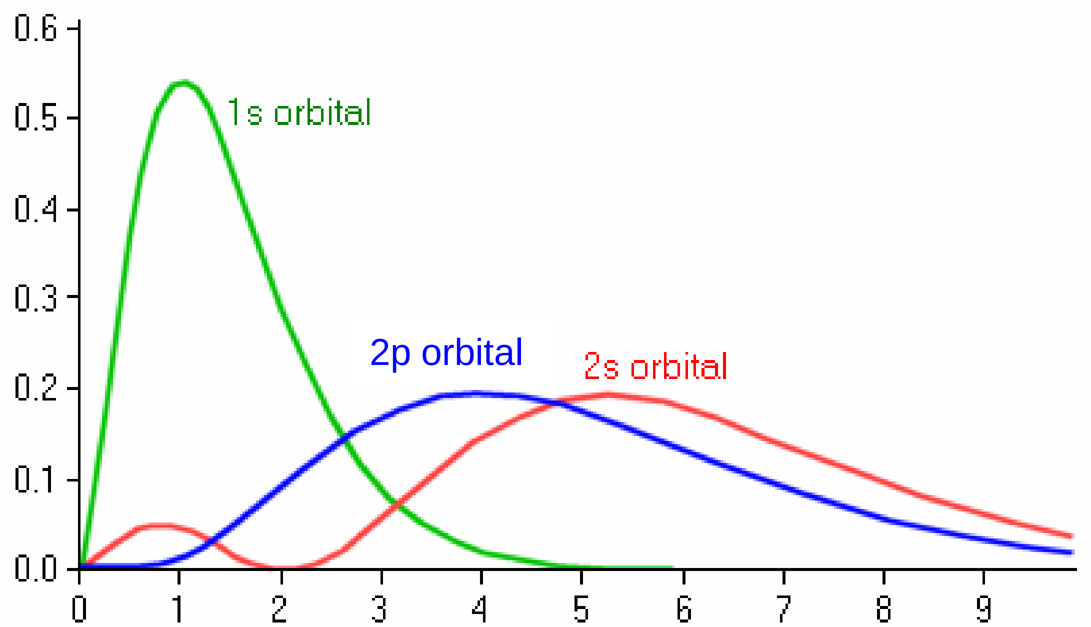


FIGURE 4.6: Surfaces of constant $|\psi|^2$ for the first few hydrogen wave functions. Reprinted by permission from Siegmund Brandt and Hans Dieter Dahmen, *The Picture Book of Quantum Mechanics*, 3rd ed., Springer, New York (2001).

For the hydrogen atom

The integrated probability density in a spherical shell with radius *r* and thickness *dr*



r in units of the Bohr radius

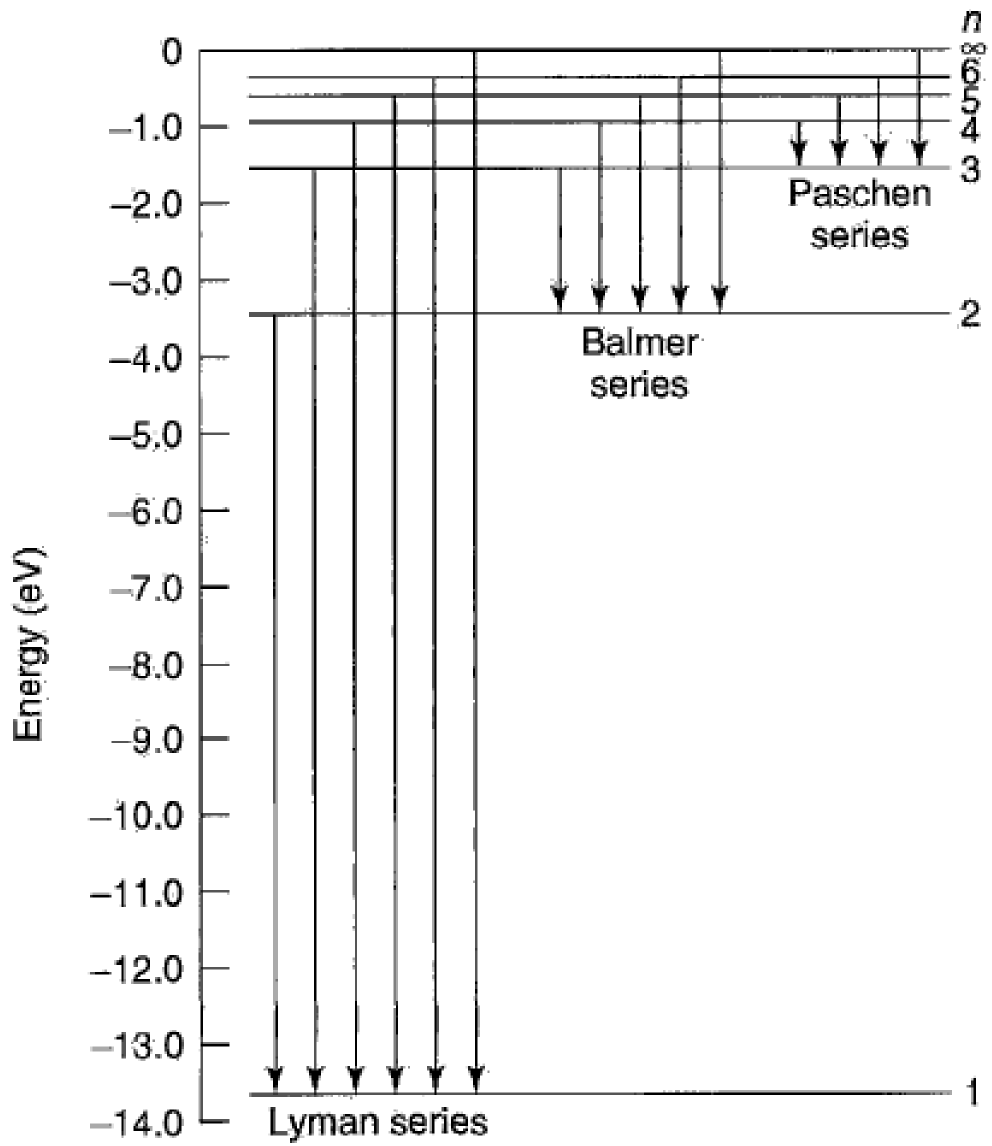


FIGURE 4.7: Energy levels and transitions in the spectrum of hydrogen.