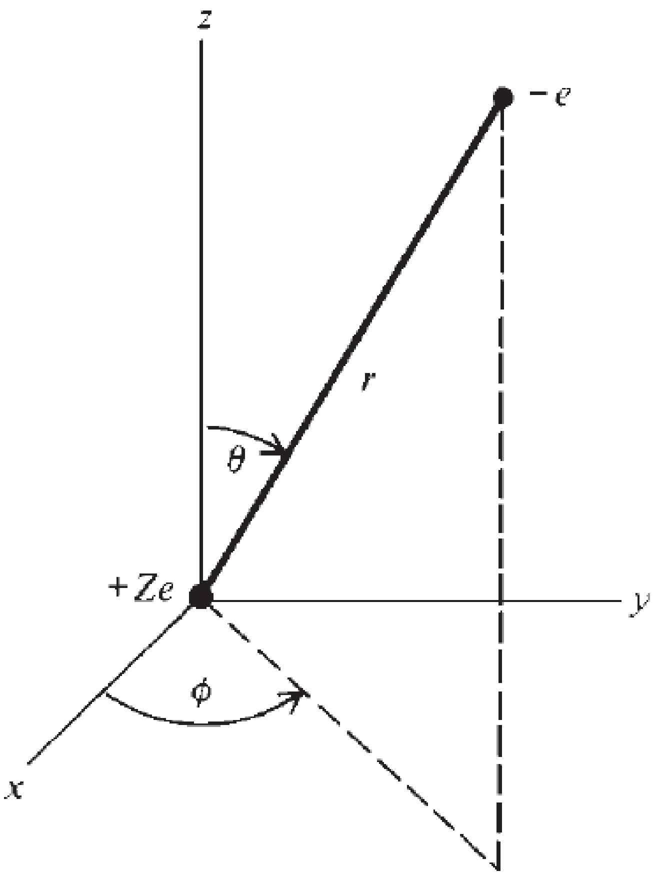
Átomo de Hidrogênio



$$V(r) = -\frac{e^2}{4\pi\varepsilon_0 r}$$

equação de Schrödinger:

$$\hat{H}\psi = E\psi$$

$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

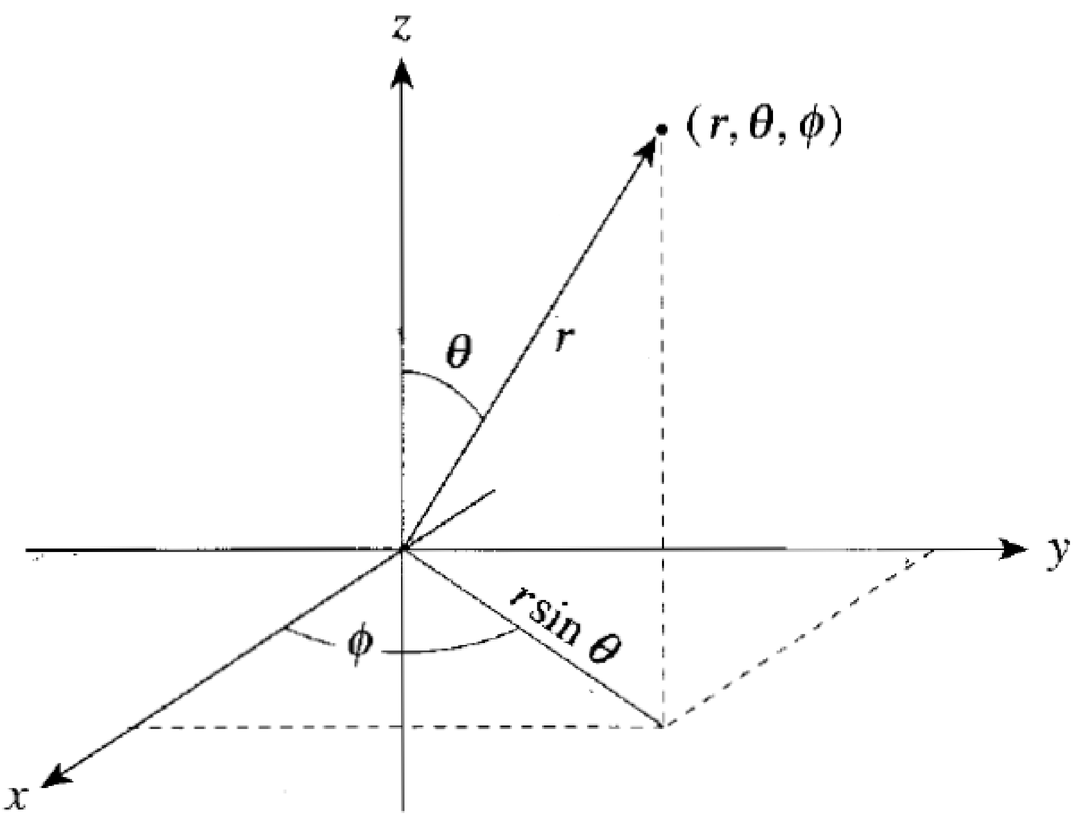
$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

$$r = \sqrt{x^2 + y^2 + z^2}$$

$$x = r\sin\theta\cos\phi \qquad r = \left(x^2 + y^2 + z^2\right)^{1/2}$$

$$y = r\sin\theta\sin\phi \qquad \cos\theta = \frac{z}{(x^2 + y^2 + z^2)^{1/2}}$$

$$z = r\cos\theta \qquad \tan\phi = \frac{y}{x}$$



$$\hat{H} = -\frac{\hbar^2}{2m_e}\nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)_{\theta,\phi} + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)_{r,\phi} + \frac{1}{r^2\sin^2\theta}\left(\frac{\partial^2}{\partial\phi^2}\right)_{r,\theta}$$

$\hbar^2 l(l+1)$

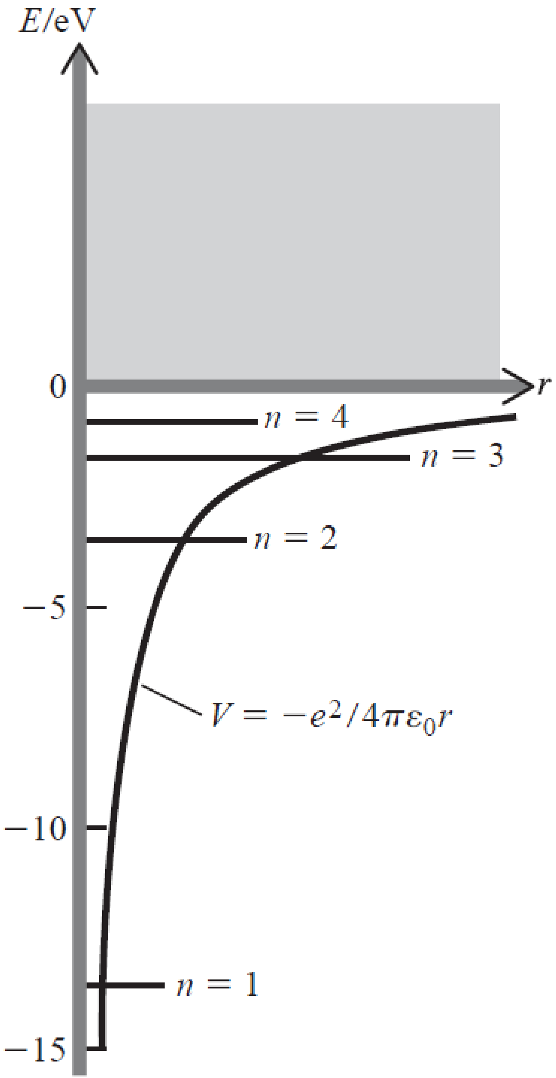
$$-\frac{\hbar^2}{2m_e}\left[\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial\psi}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2\psi}{\partial\phi^2}\right] - \frac{e^2}{4\pi\varepsilon_0 r}\psi(r,\theta,\phi) = E\psi(r,\theta,\phi)$$

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi)$$

$$V_{eff} = -\frac{e^2}{4\pi\varepsilon_o r} + \frac{\hbar^2 l(l+1)}{2m_e r^2}$$

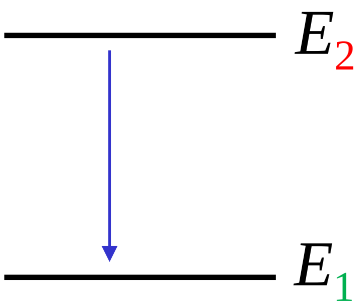
$$-\frac{\hbar^2}{2m_e r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[\frac{\hbar^2 l(l+1)}{2m_e r^2} - \frac{e^2}{4\pi\varepsilon_0 r}\right]R(r) = E\,R(r)$$

Níveis de energia do átomo de hidrogênio



$$E_n = -\frac{1}{n^2}\frac{m_e e^4}{8\varepsilon_0^2 h^2} \qquad n = 1, 2, 3, 4 \ldots$$

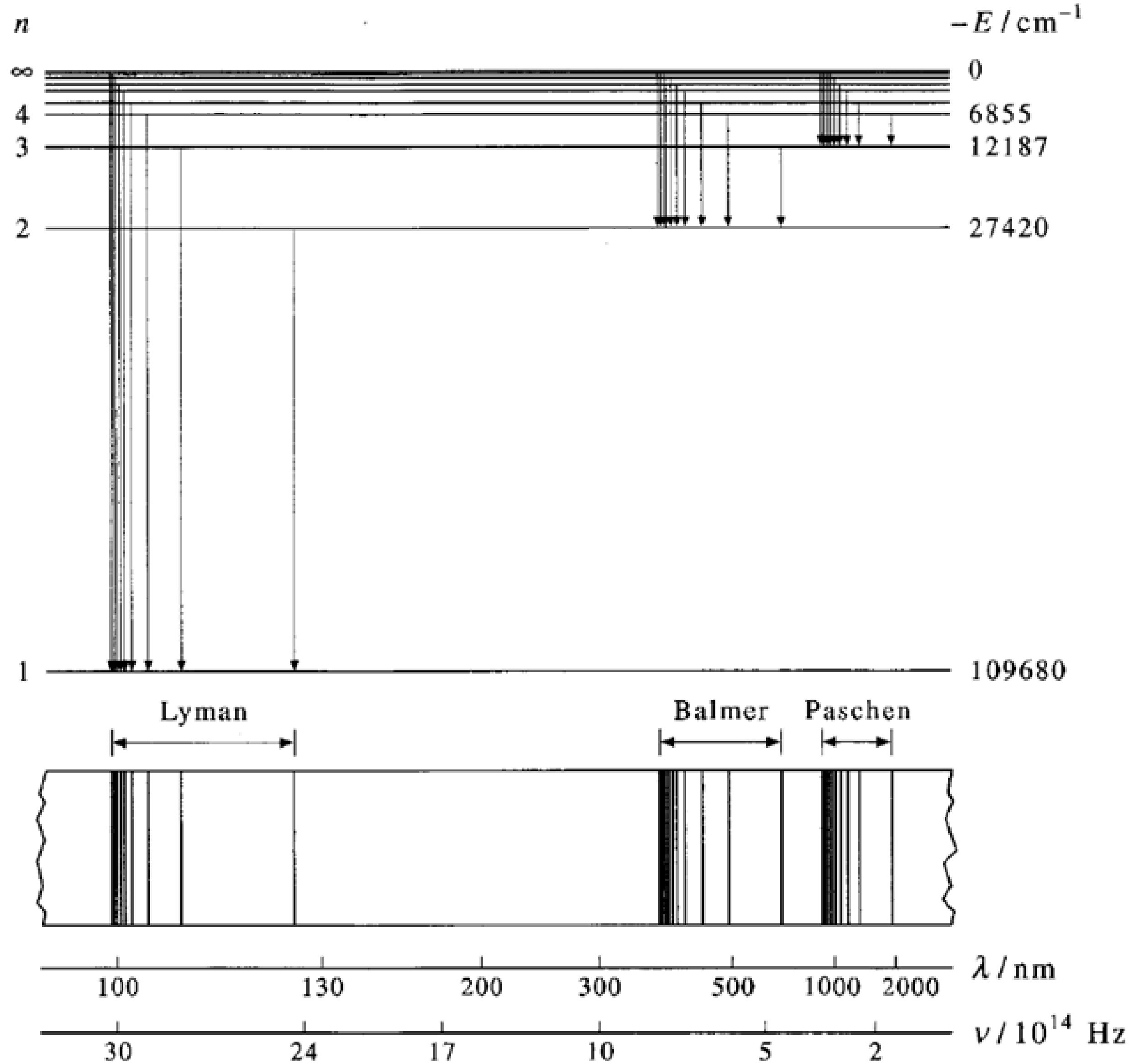
$$\frac{m_e e^4}{8\varepsilon_0^2 h^2} = R_H \quad \textit{constante de Rydberg}$$



$$\Delta E = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

$$\parallel$$

energia da radiação $E = h\nu = hc\frac{1}{\lambda} = hc\tilde{\nu}$



n
$-E / cm^{-1}$
∞
0
4
6855
3
12187
2
27420
1
109680
Lyman
Balmer
Paschen
λ / nm
100
130
200
300
500
1000
2000
$\nu / 10^{14}$ Hz
30
24
17
10
5
2

Funções de onda do átomo de hidrogênio

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

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

$$l = 0, 1, 2, \ldots, n-1$$

$$m = -l, -l+1, \ldots, l-1, l$$

$n =$	1	2	3	4 ...
	K	L	M	N ...

$l =$	0	1	2	3
	s	p	d	f

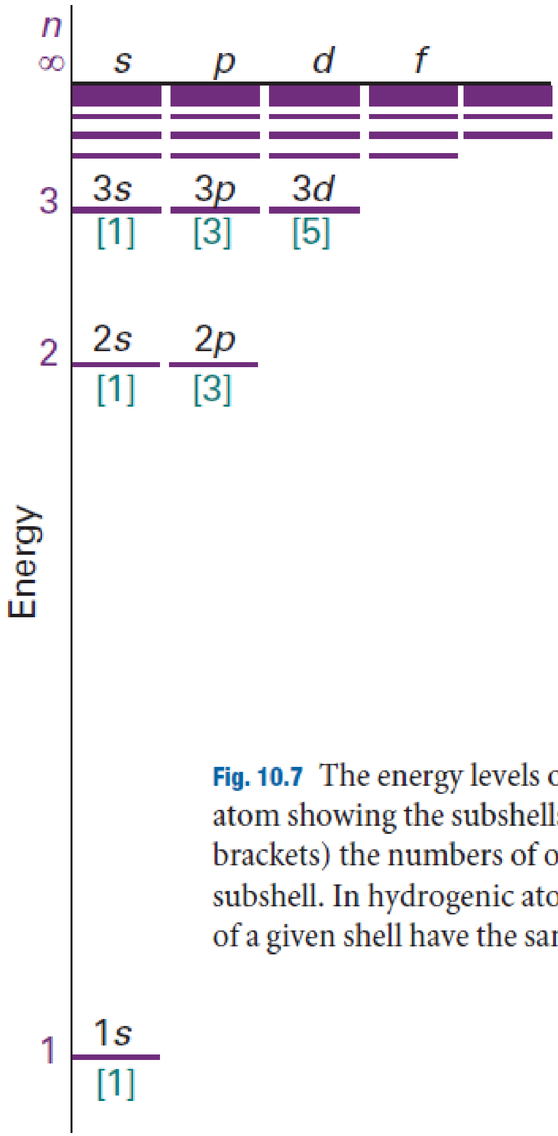


Fig. 10.7 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy.

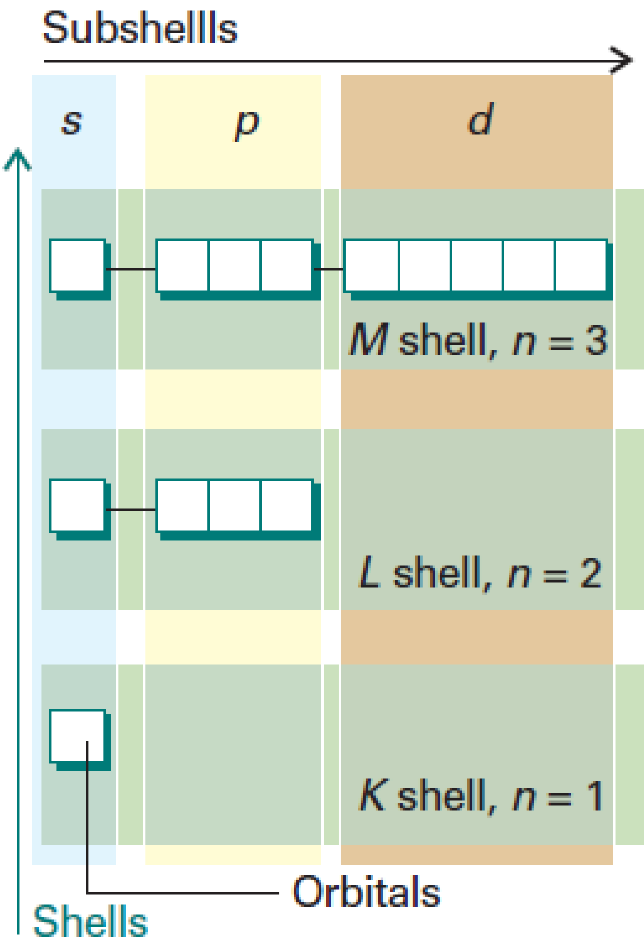


Fig. 10.8 The organization of orbitals (white squares) into subshells (characterized by l) and shells (characterized by n).

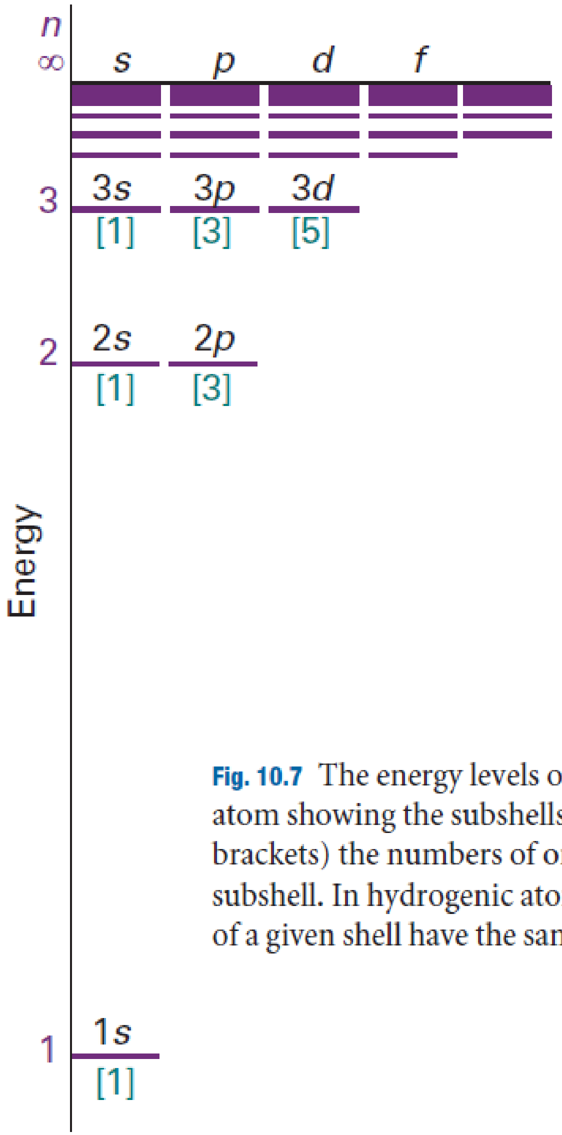
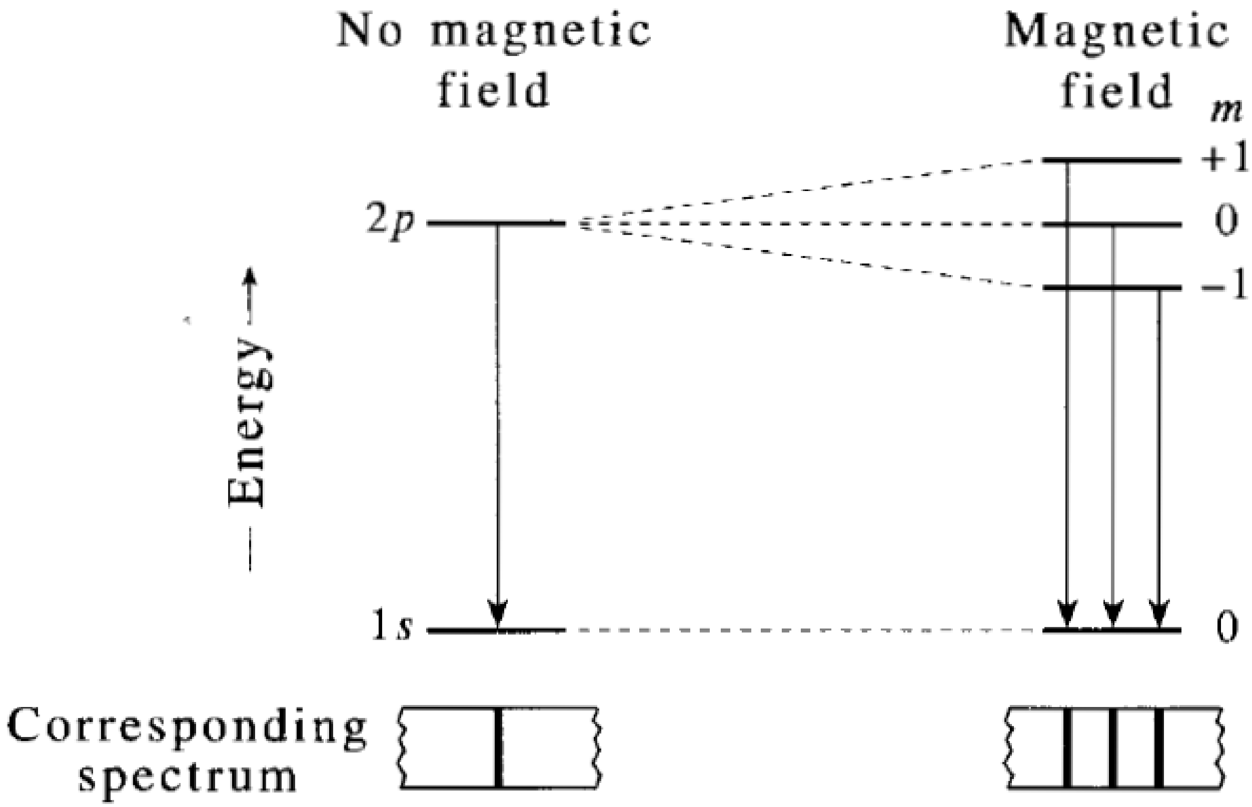


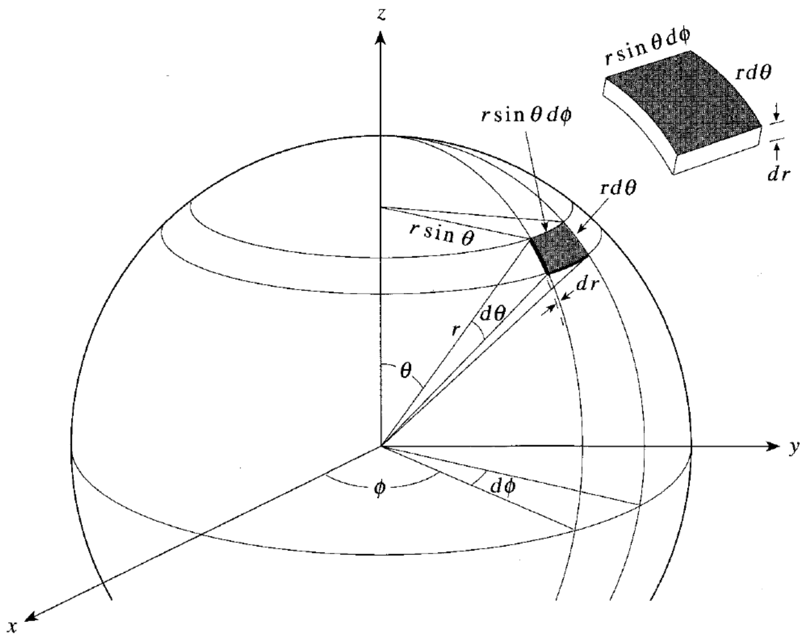
Fig. 10.7 The energy levels of the hydrogen atom showing the subshells and (in square brackets) the numbers of orbitals in each subshell. In hydrogenic atoms, all orbitals of a given shell have the same energy.



No magnetic field
Magnetic field
m
+1
0
−1
0
2p
1s
Energy
Corresponding spectrum

The complete hydrogenlike atomic wave functions for $n = 1, 2$, and 3. The quantity Z is the atomic number of the nucleus, and $\sigma = Zr/a_0$, where a_0 is the Bohr radius. $a_0 = \hbar^2(4\pi\varepsilon_0)/m_e e^2 = 0.5292$ Å

$n = 1,$	$l = 0,$	$m = 0$	$\psi_{100} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2,$	$l = 0,$	$m = 0$	$\psi_{200} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
	$l = 1,$	$m = 0$	$\psi_{210} = \dfrac{1}{\sqrt{32\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta$
	$l = 1,$	$m = \pm 1$	$\psi_{21\pm1} = \dfrac{1}{\sqrt{64\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta e^{\pm i\phi}$
$n = 3,$	$l = 0,$	$m = 0$	$\psi_{300} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
	$l = 1,$	$m = 0$	$\psi_{310} = \dfrac{1}{81}\left(\dfrac{2}{\pi}\right)^{1/2}\left(\dfrac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3}\cos\theta$
	$l = 1,$	$m = \pm 1$	$\psi_{31\pm1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (6\sigma - \sigma^2)e^{-\sigma/3}\sin\theta e^{\pm i\phi}$
	$l = 2,$	$m = 0$	$\psi_{320} = \dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
	$l = 2,$	$m = \pm 1$	$\psi_{32\pm1} = \dfrac{1}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta e^{\pm i\phi}$
	$l = 2,$	$m = \pm 2$	$\psi_{32\pm2} = \dfrac{1}{162\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta e^{\pm 2i\phi}$



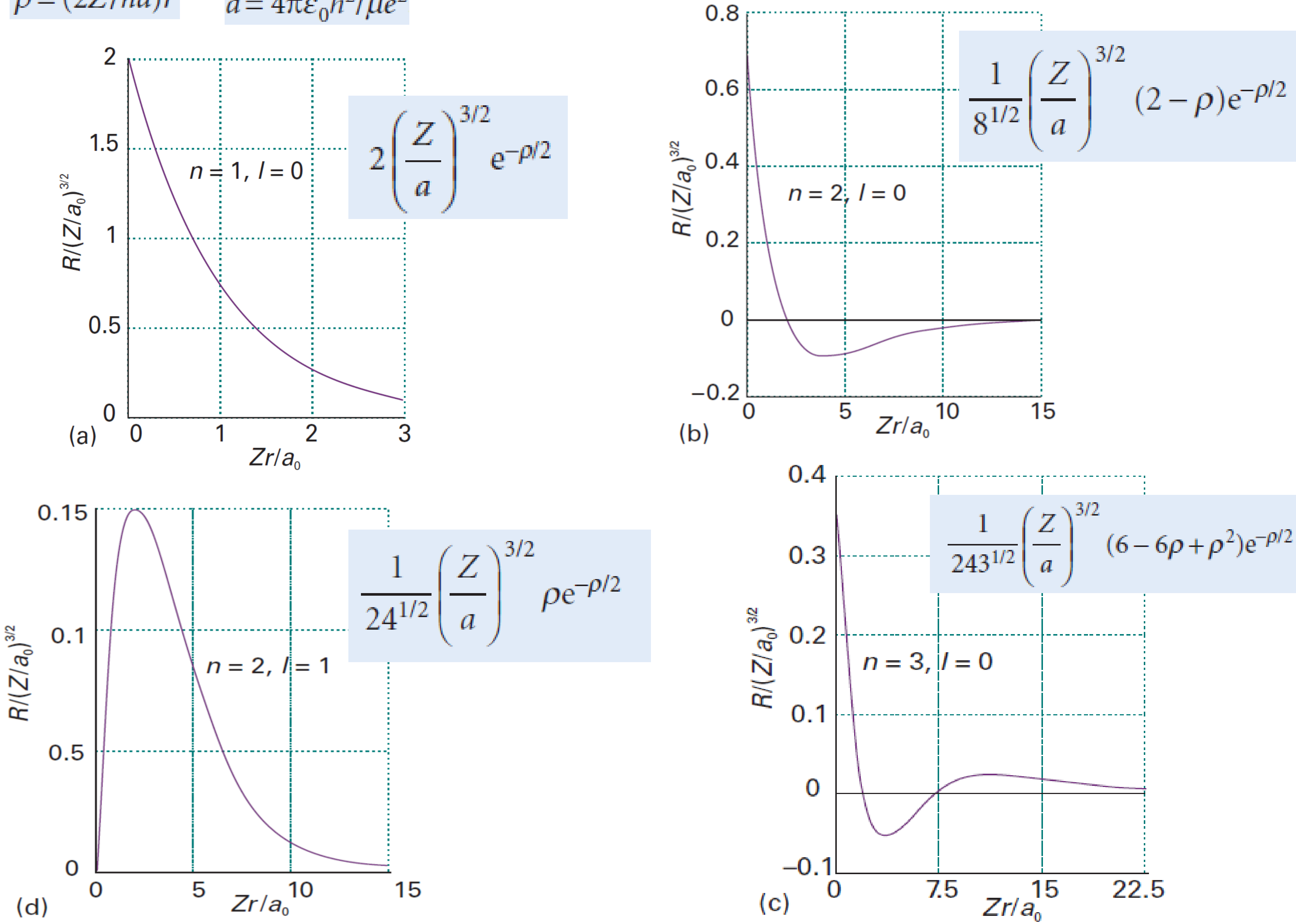
volume element $r^2 \sin\theta \, dr \, d\theta \, d\phi$

$$0 \leq r \leq \infty, \quad 0 \leq \theta \leq \pi, \quad 0 \leq \phi \leq 2\pi$$

normalização das autofunções:

$$\int_0^\infty dr\, r^2 \int_0^\pi d\theta \sin\theta \int_0^{2\pi} d\phi\, \psi_{nlm}^*(r,\theta,\phi)\psi_{nlm}(r,\theta,\phi) = 1$$

$\rho = (2Z/na)r$ $a = 4\pi\varepsilon_0\hbar^2/\mu e^2$



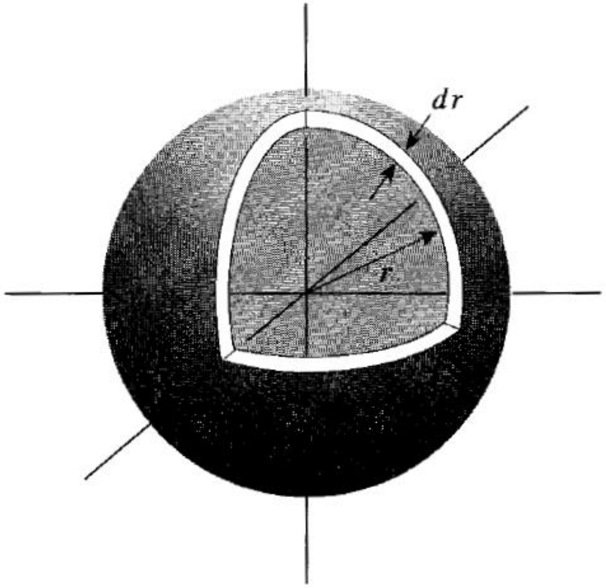
Função de distribuição radial, $P(r)\mathrm{d}r$

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

$0 \le r \le \infty, \quad 0 \le \theta \le \pi, \quad 0 \le \phi \le 2\pi$ volume element $r^2 \sin\theta\, dr\, d\theta\, d\phi$

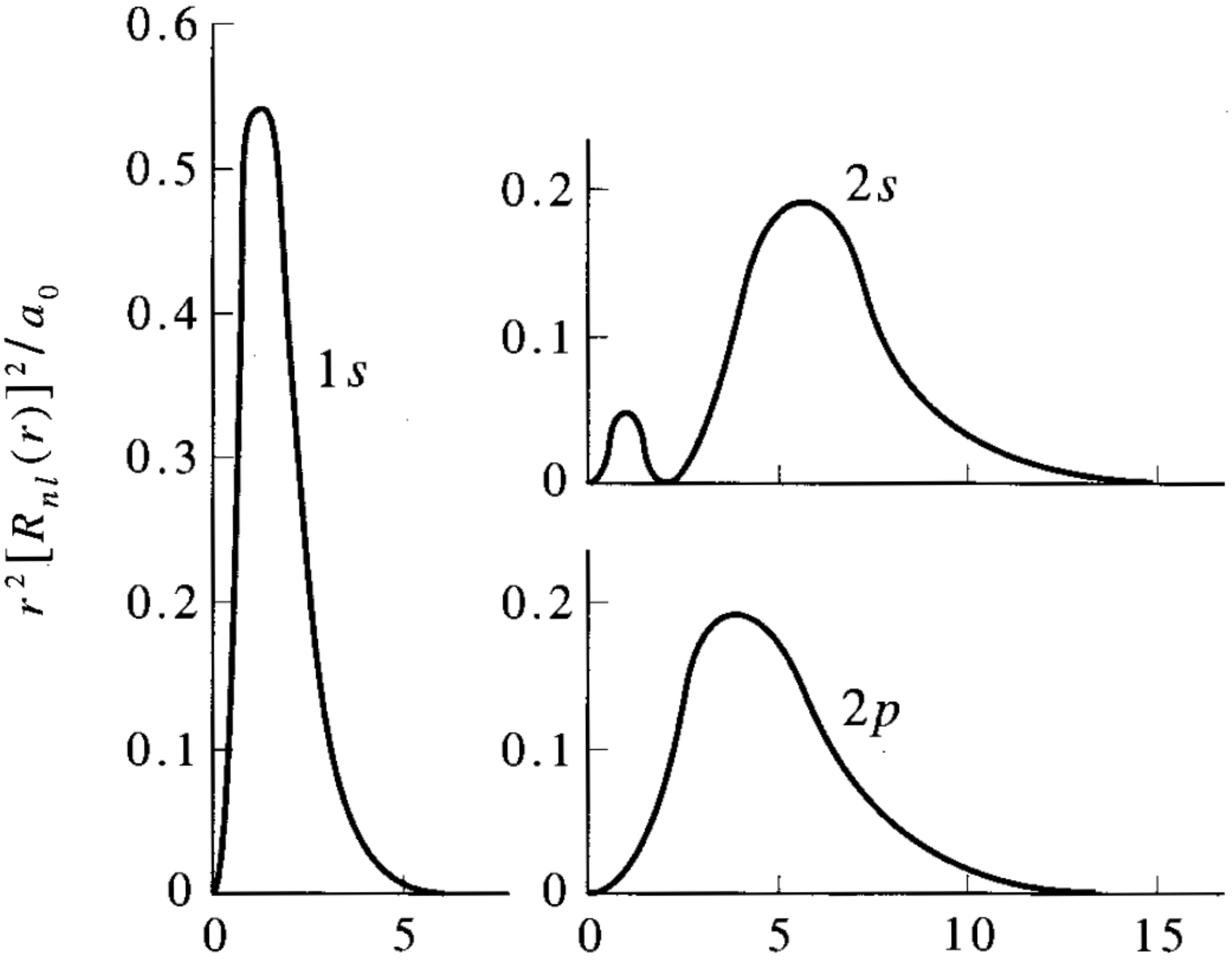
$$P(r)\mathrm{d}r = \int_0^{\pi}\int_0^{2\pi} \overbrace{R(r)^2|Y(\theta,\phi)|^2}^{\psi^2}\, \overbrace{r^2\mathrm{d}r\,\sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{\mathrm{d}\tau}$$

$$= r^2R(r)^2\mathrm{d}r\, \overbrace{\int_0^{\pi}\int_0^{2\pi} |Y(\theta,\phi)|^2 \sin\theta\,\mathrm{d}\theta\,\mathrm{d}\phi}^{1}$$

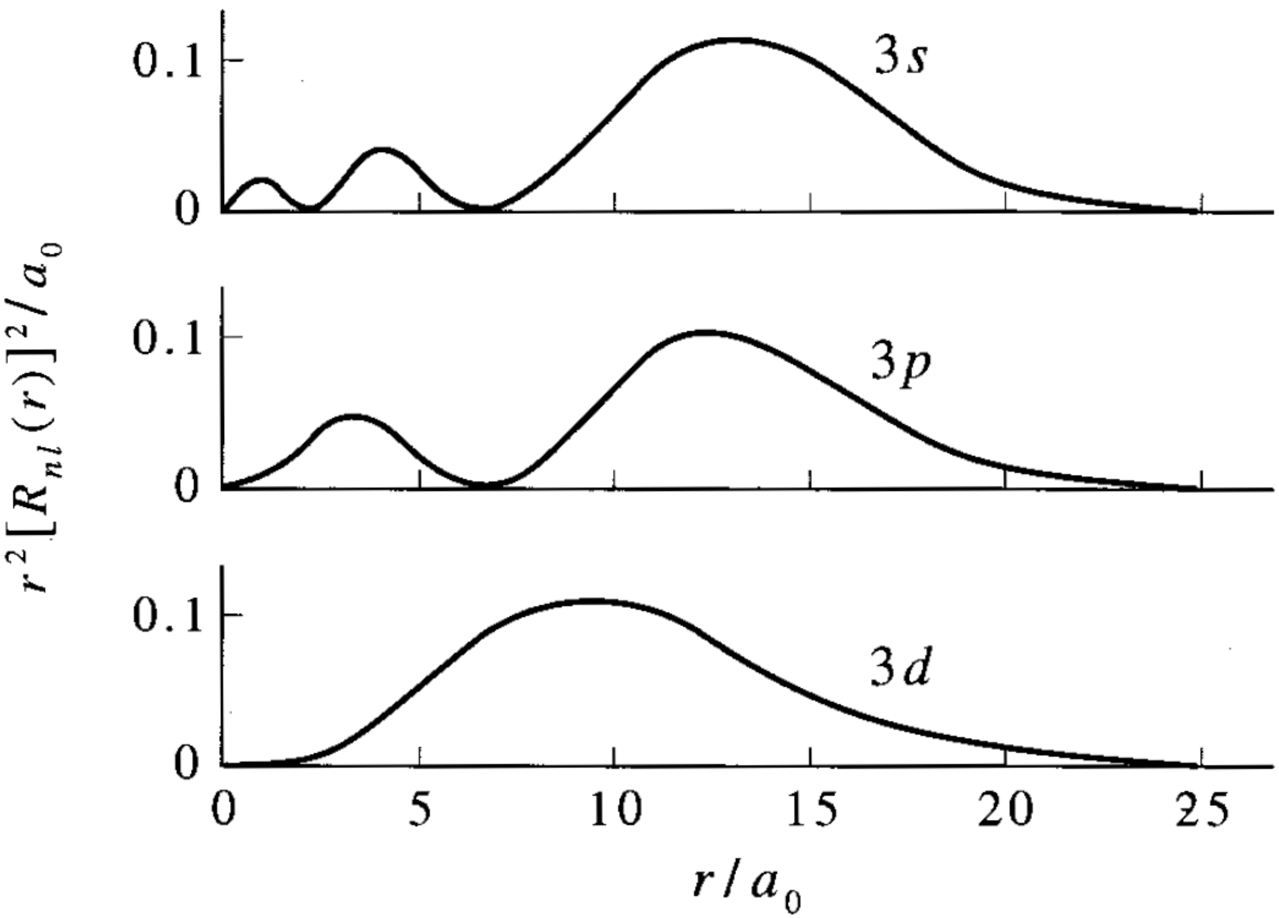


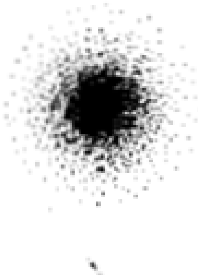
$$\boxed{P(r)\mathrm{d}r = r^2R(r)^2\mathrm{d}r}$$

Função de distribuição radial, $P(r)\mathrm{d}r$

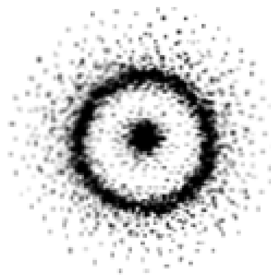


Função de distribuição radial, $P(r)\mathrm{d}r$

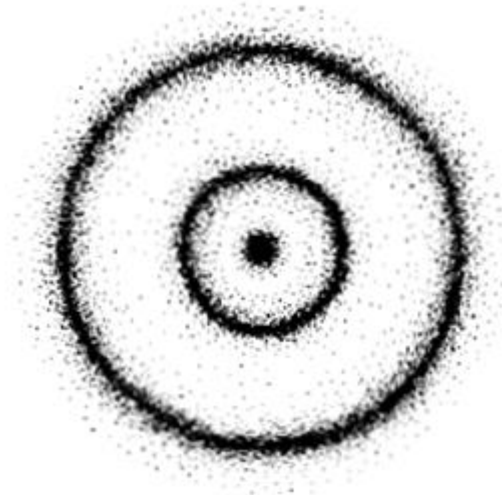




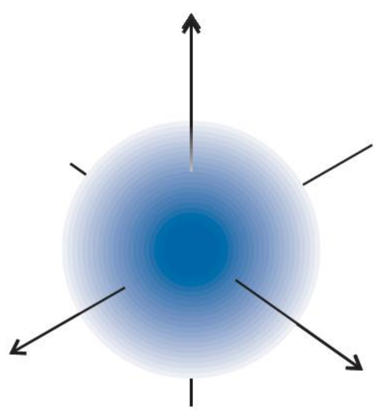
1*s*



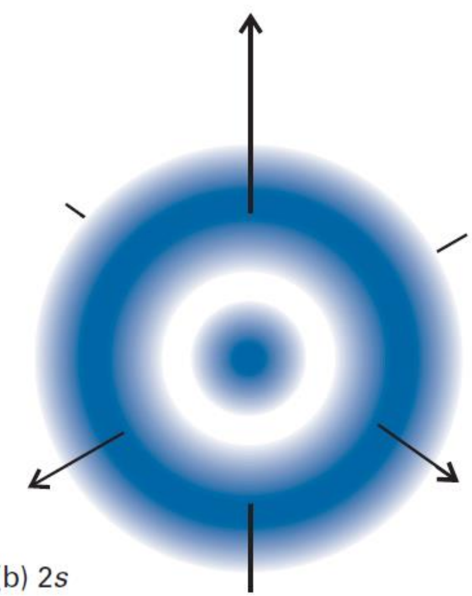
2*s*



3*s*

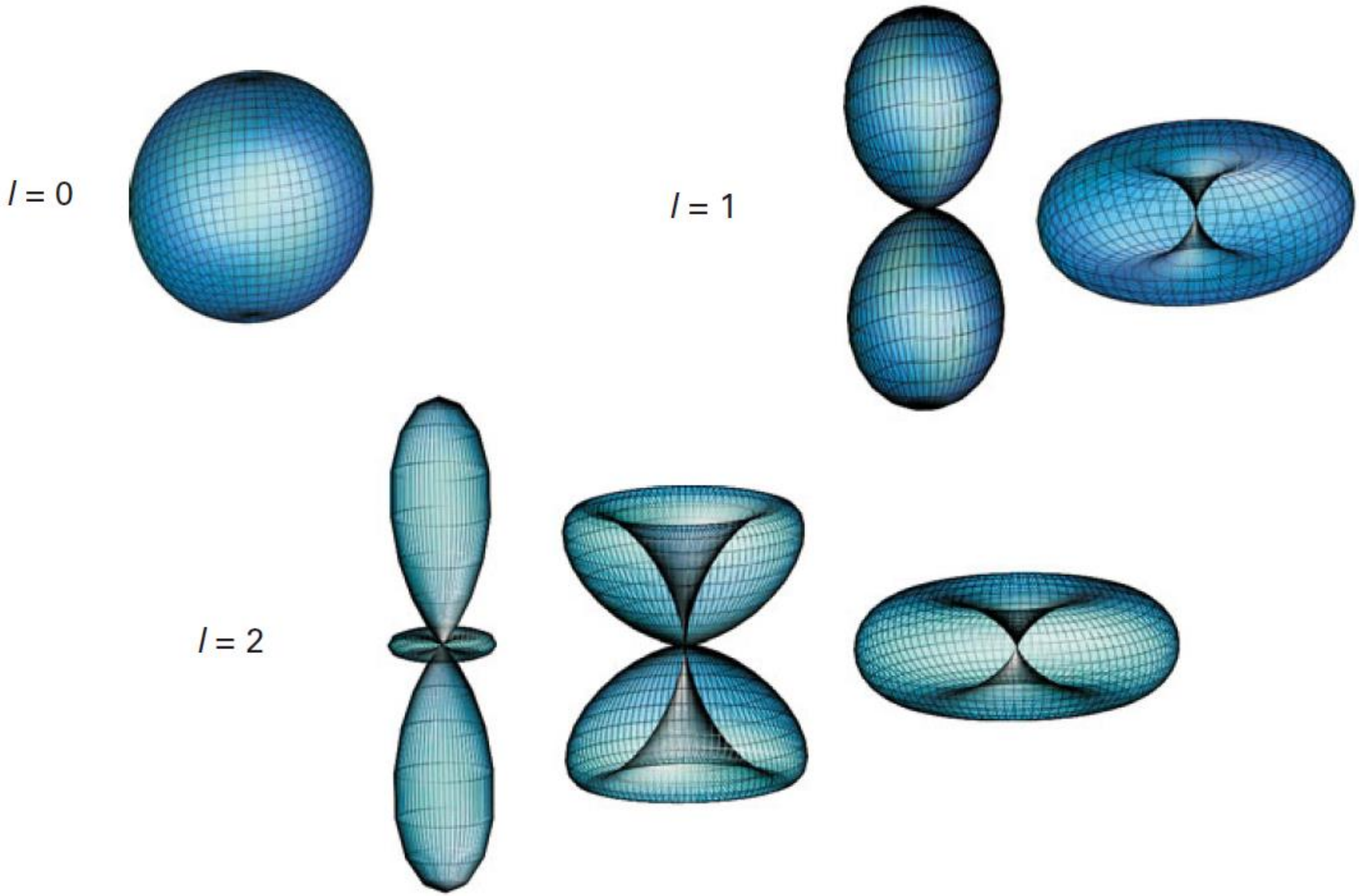


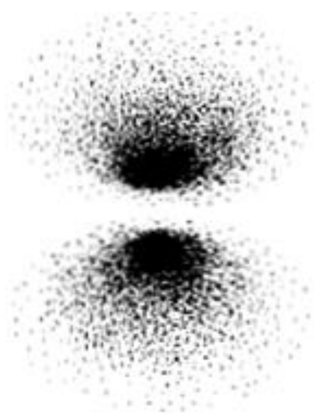
(a) 1*s*



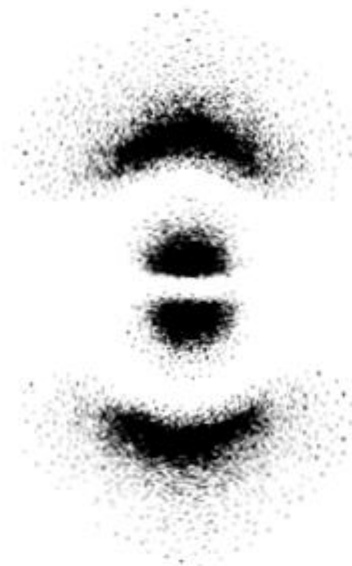
(b) 2*s*

Harmônicos Esféricos

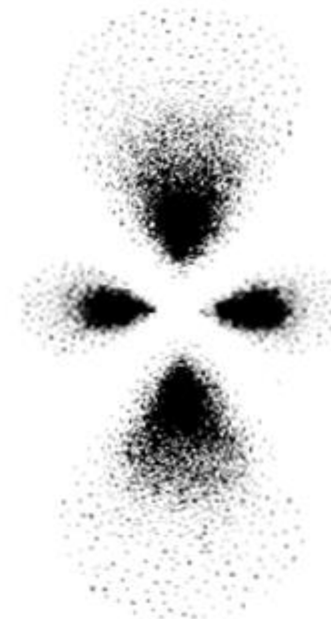




$2p_0$

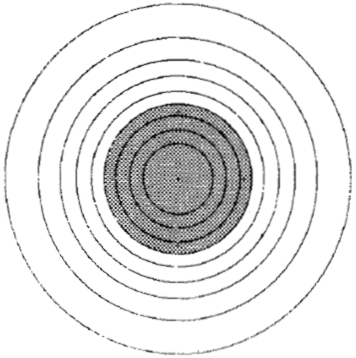


$3p_0$

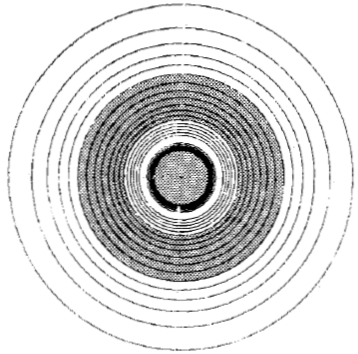


$3d_0$

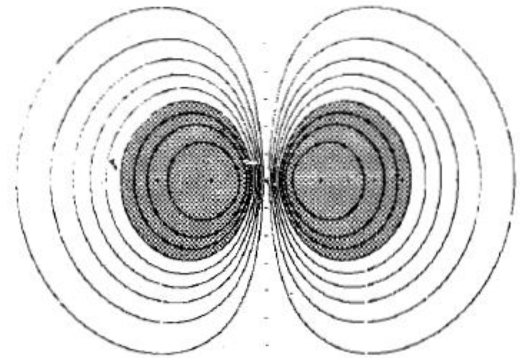
Mapas de contorno de probabilidade



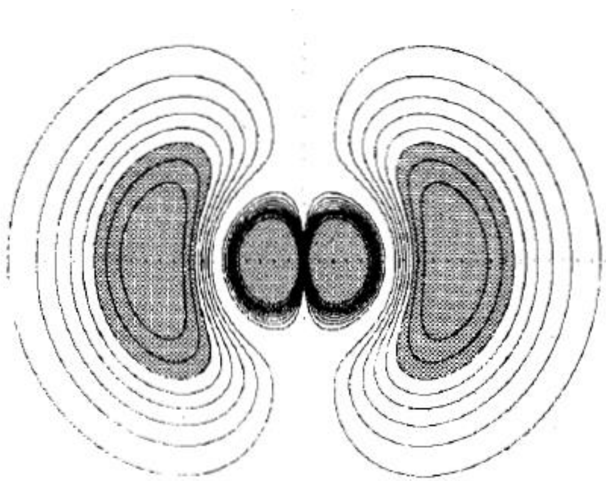
(a) 1s



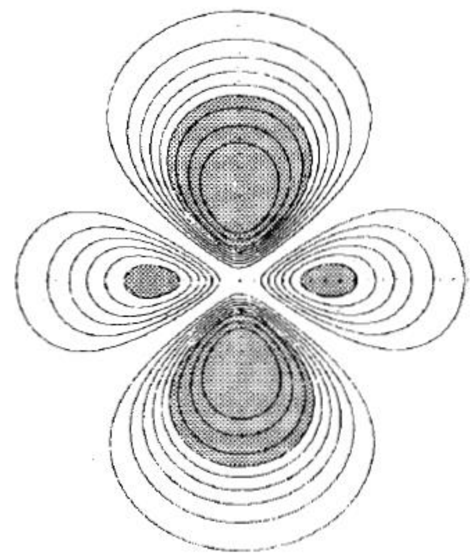
(b) 2s



(d) $2p_0$



(e) $3p_0$



(f) $3d_0$

Funções de onda reais

$$x = r \sin\theta \cos\phi$$

$$y = r \sin\theta \sin\phi$$

$$z = r \cos\theta$$

$$2p_0 = ce^{-Zr/2a} r \cos\theta \Rightarrow 2p_z \equiv 2p_0 = cze^{-Zr/2a}$$

$$2p_{+1} = be^{-Zr/2a} r \sin\theta\, e^{i\phi}$$

$$2p_{-1} = be^{-Zr/2a} r \sin\theta\, e^{-i\phi}$$

$$2p_x \equiv (2p_1 + 2p_{-1})/\sqrt{2} \Rightarrow 2p_x = cxe^{-Zr/2a}$$

$$2p_y \equiv (2p_1 - 2p_{-1})/i\sqrt{2} \Rightarrow 2p_y = cye^{-Zr/2a}$$

$$e^{i\phi} = \cos\phi + i \sin\phi$$

Funções de onda reais

$$p_x = \frac{1}{\sqrt{2}}(Y_1^1 + Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\cos\phi$$

$$p_y = \frac{1}{\sqrt{2}i}(Y_1^1 - Y_1^{-1}) = \left(\frac{3}{4\pi}\right)^{1/2} \sin\theta\sin\phi$$

$$d_{z^2} = Y_2^0 = \left(\frac{5}{16\pi}\right)^{1/2} (3\cos^2\theta - 1)$$

$$d_{xz} = \frac{1}{\sqrt{2}}(Y_2^1 + Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\cos\phi$$

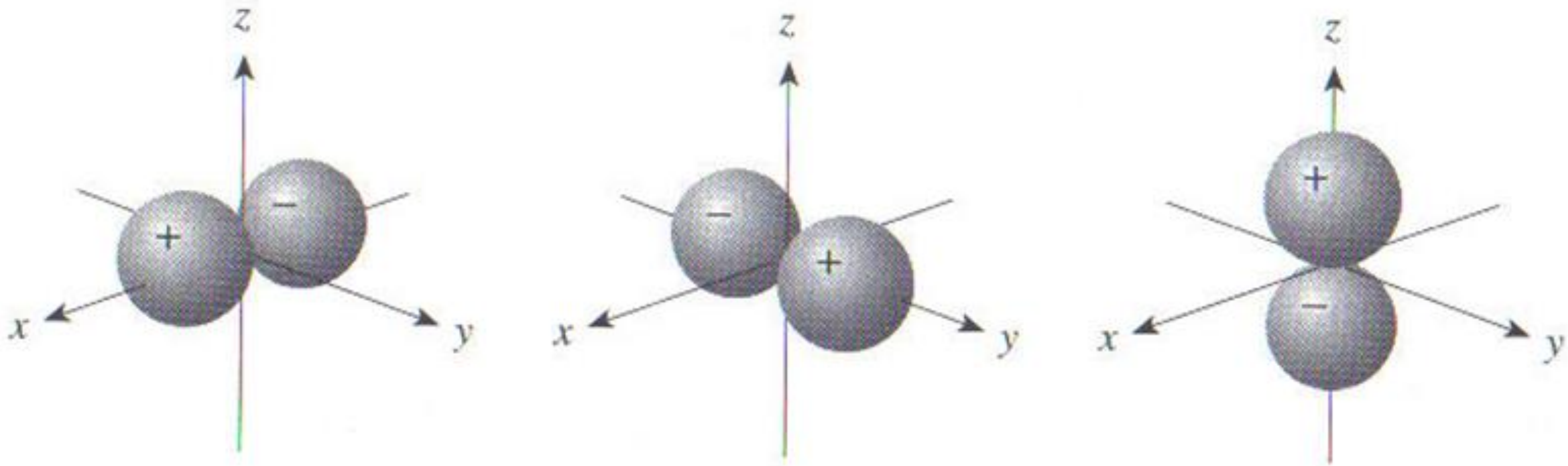
$$d_{yz} = \frac{1}{\sqrt{2}i}(Y_2^1 - Y_2^{-1}) = \left(\frac{15}{4\pi}\right)^{1/2} \sin\theta\cos\theta\sin\phi$$

$$d_{x^2-y^2} = \frac{1}{\sqrt{2}}(Y_2^2 + Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\cos 2\phi$$

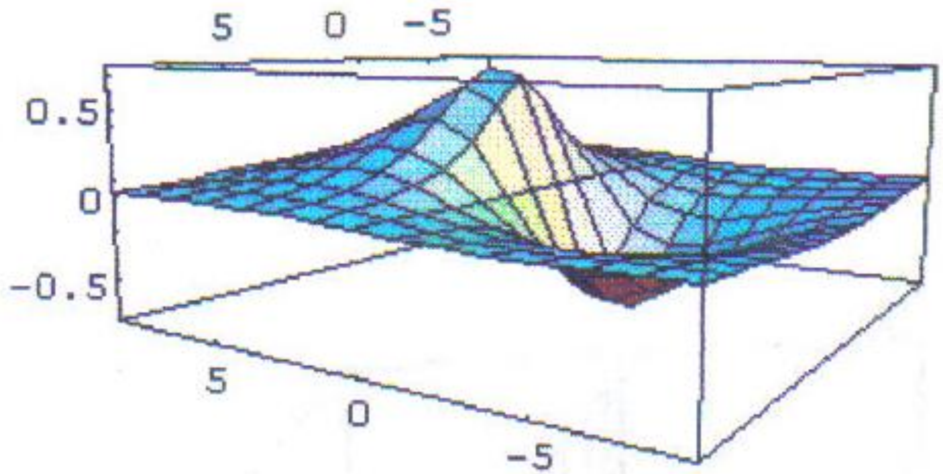
$$d_{xy} = \frac{1}{\sqrt{2}i}(Y_2^2 - Y_2^{-2}) = \left(\frac{15}{16\pi}\right)^{1/2} \sin^2\theta\sin 2\phi$$

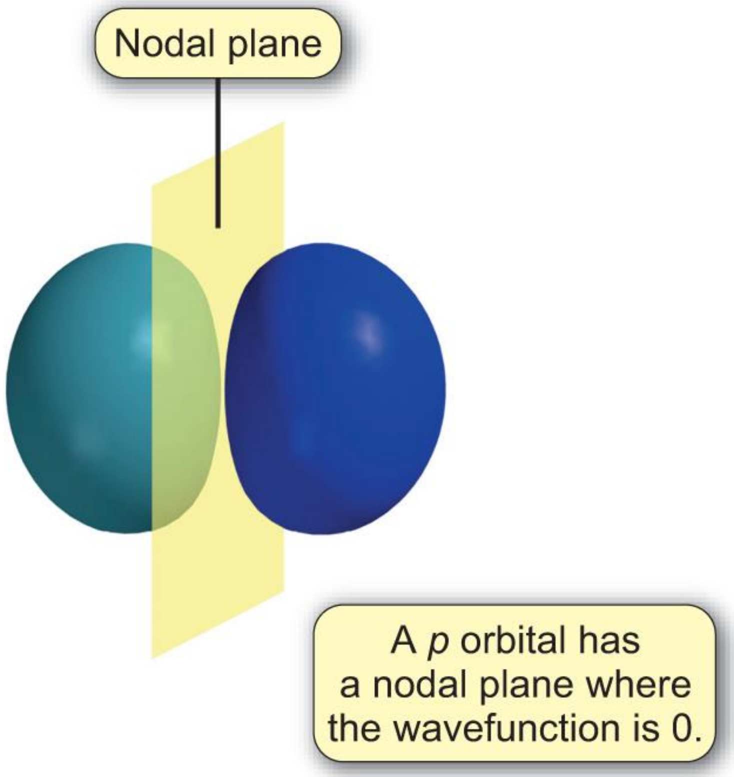
The complete hydrogenlike atomic wave functions expressed as real functions for $n = 1, 2,$ and 3. The quantity Z is the atomic number of the nucleus and $\sigma = Zr/a_0$, where a_0 is the Bohr radius.

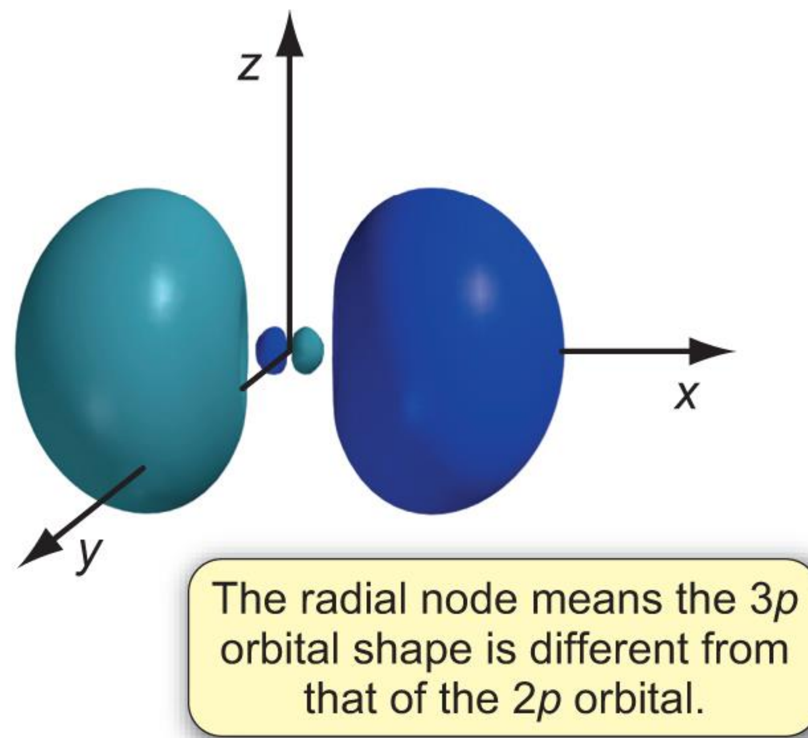
$n = 1,$	$l = 0,$	$m = 0$	$\psi_{1s} = \dfrac{1}{\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} e^{-\sigma}$
$n = 2,$	$l = 0,$	$m = 0$	$\psi_{2s} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (2-\sigma)e^{-\sigma/2}$
	$l = 1,$	$m = 0$	$\psi_{2p_z} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\cos\theta$
	$l = 1,$	$m = \pm 1$	$\psi_{2p_x} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta\cos\phi$
			$\psi_{2p_y} = \dfrac{1}{4\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma e^{-\sigma/2}\sin\theta\sin\phi$
$n = 3,$	$l = 0,$	$m = 0$	$\psi_{3s} = \dfrac{1}{81\sqrt{3\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} (27 - 18\sigma + 2\sigma^2)e^{-\sigma/3}$
	$l = 1,$	$m = 0$	$\psi_{3p_z} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\cos\theta$
	$l = 1,$	$m = \pm 1$	$\psi_{3p_x} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\sin\theta\cos\phi$
			$\psi_{3p_z} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma(6-\sigma)e^{-\sigma/3}\sin\theta\sin\phi$
	$l = 2,$	$m = 0$	$\psi_{3d_{z^2}} = \dfrac{1}{81\sqrt{6\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}(3\cos^2\theta - 1)$
	$l = 2,$	$m = \pm 1$	$\psi_{3d_{xy}} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\cos\phi$
			$\psi_{3d_{yz}} = \dfrac{\sqrt{2}}{81\sqrt{\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin\theta\cos\theta\sin\phi$
	$l = 2,$	$m = \pm 2$	$\psi_{3d_{x^2-y^2}} = \dfrac{1}{81\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta\cos 2\phi$
			$\psi_{3d_{xy}} = \dfrac{1}{81\sqrt{2\pi}}\left(\dfrac{Z}{a_0}\right)^{3/2} \sigma^2 e^{-\sigma/3}\sin^2\theta\sin 2\phi$

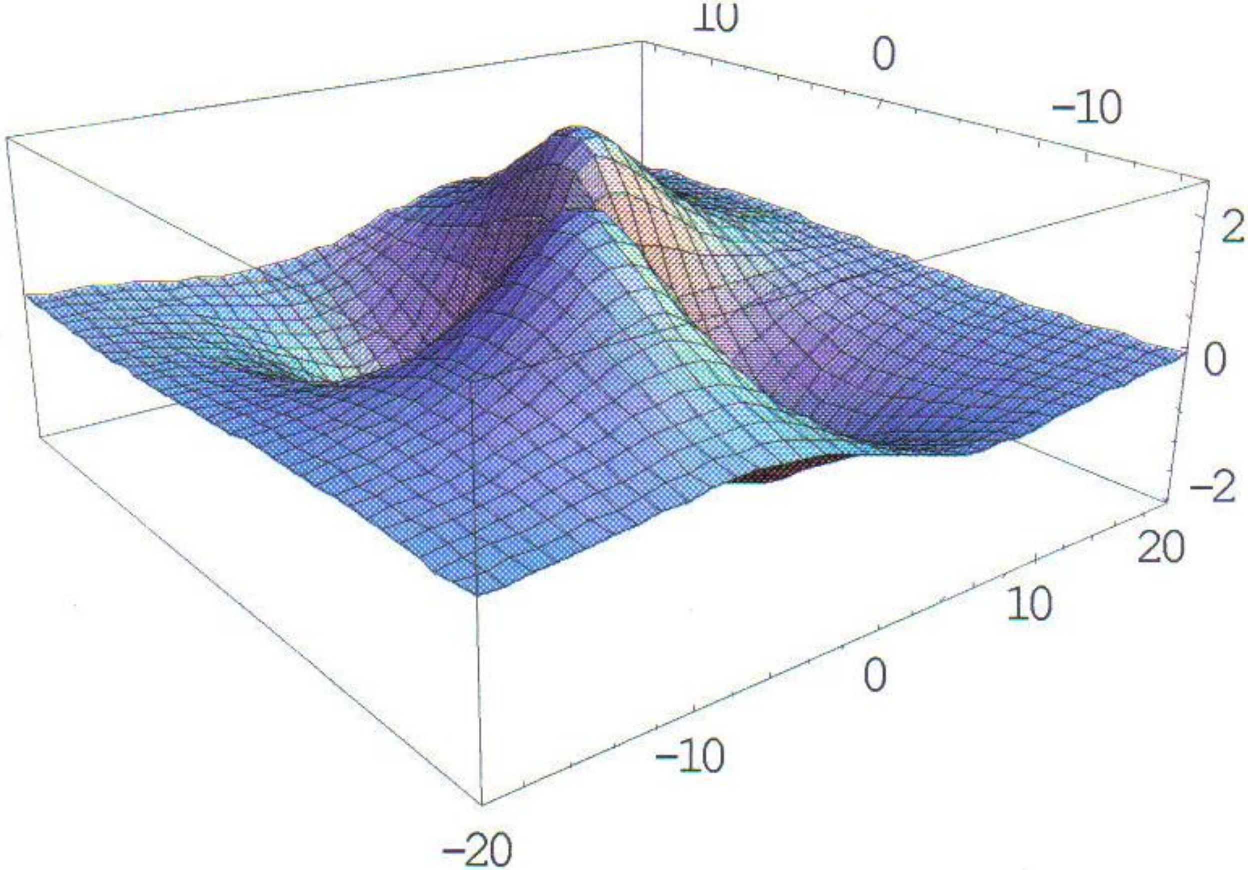


p_x p_y p_z




Nodal plane
A *p* orbital has
a nodal plane where
the wavefunction is 0.


z
x
y
The radial node means the 3*p*
orbital shape is different from
that of the 2*p* orbital.

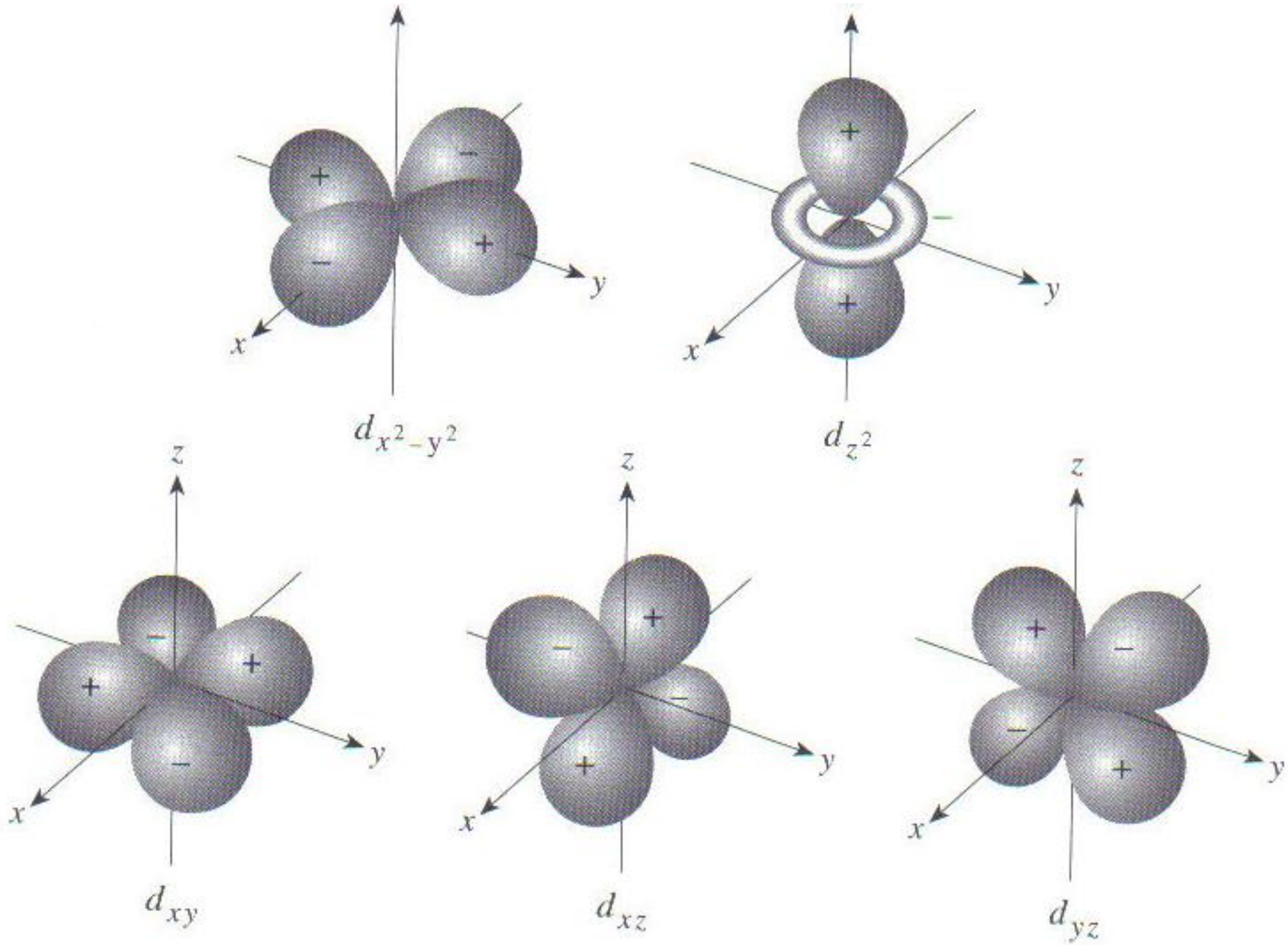


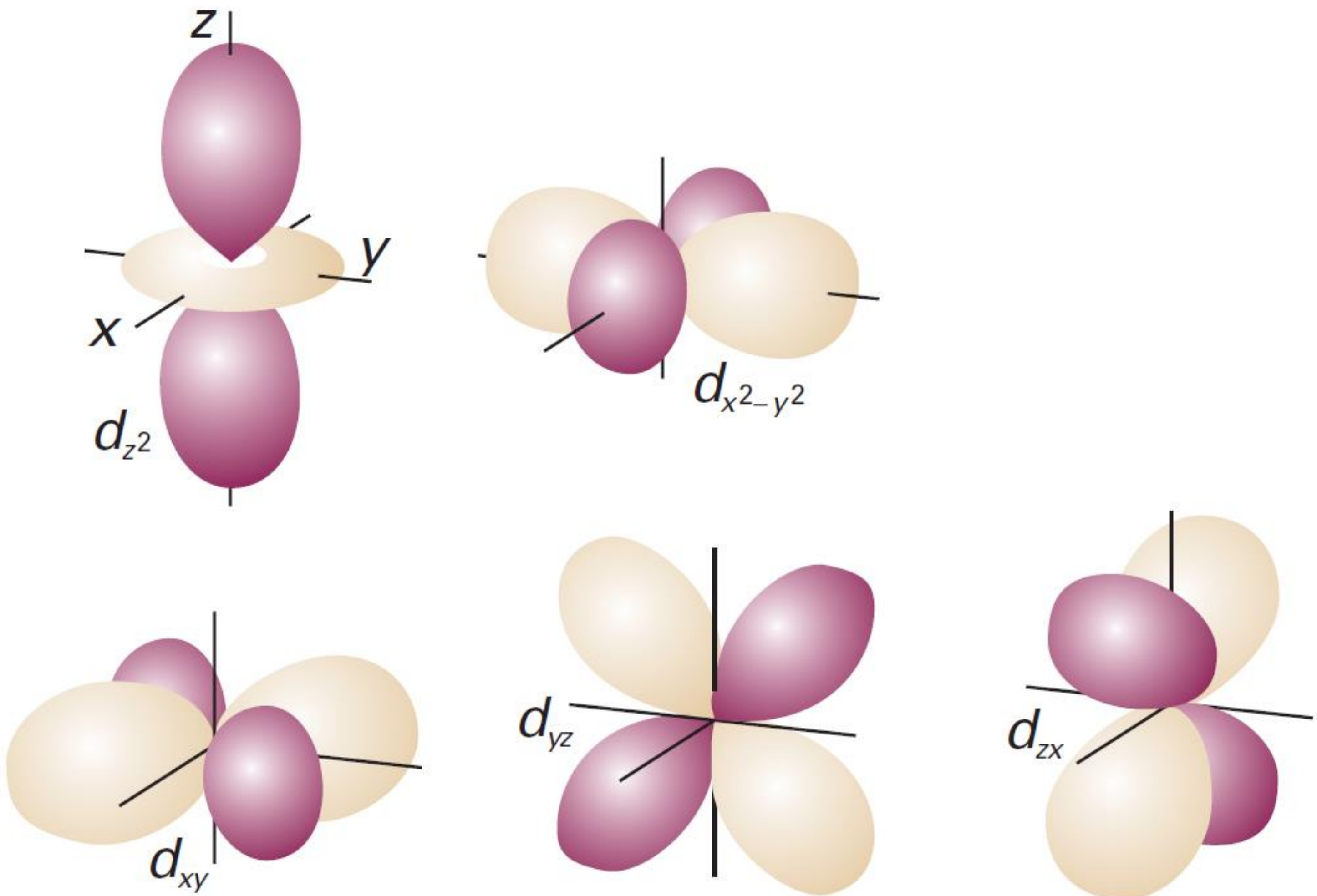
$x = r\, sen\theta \cos\phi$
$y = r\, sen\theta\, sen\phi$
$z = r \cos\phi$

$r = (x^2 + y^2 + z^2)^{½}$
$\cos\theta = z / (x^2 + y^2 + z^2)^{½}$
$tg\ \phi = y / x$

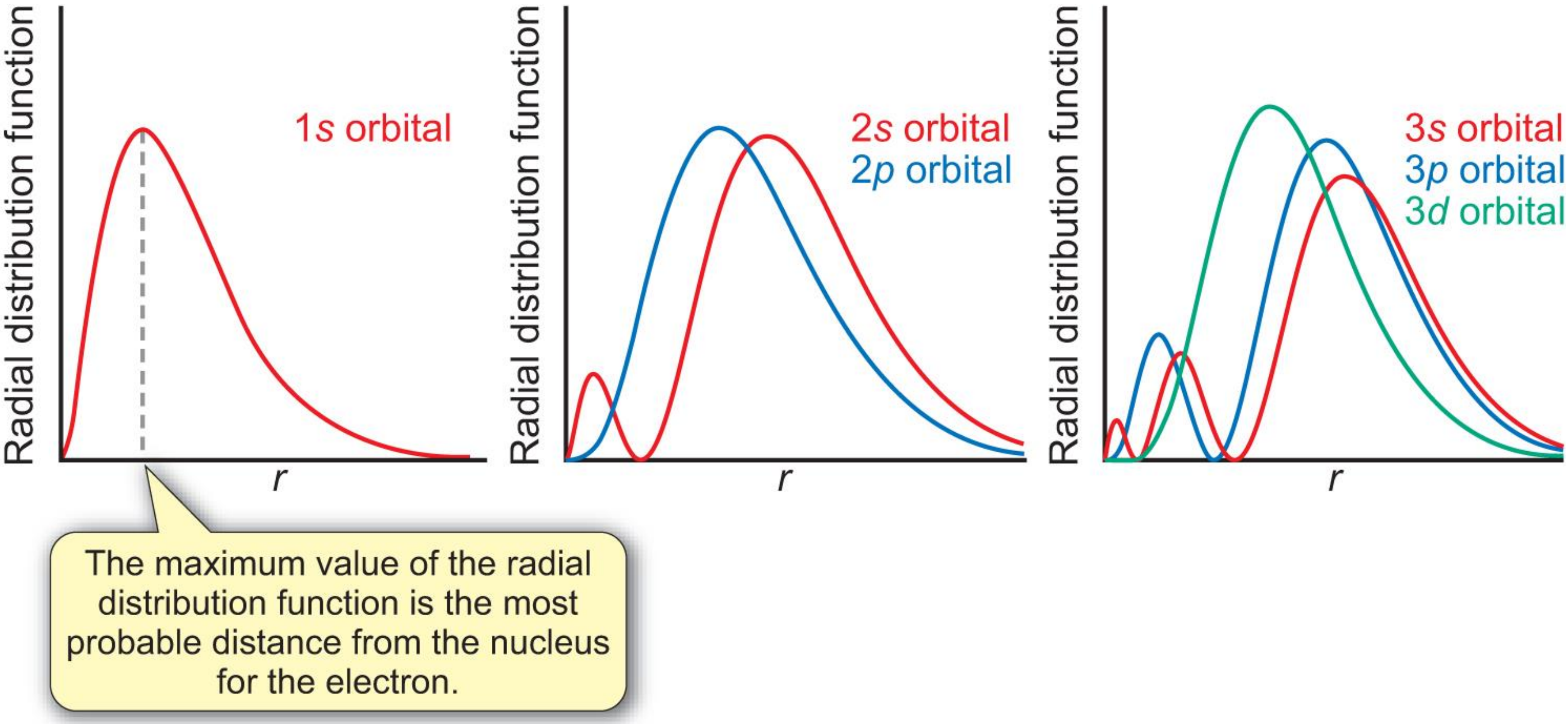
$$\psi_{3d_{xy}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a_0}\right)^{\frac{3}{2}}\left(\frac{r}{a_0}\right)^2 e^{-\frac{r}{3a_0}} \sin\theta \cos\theta \cos\phi$$

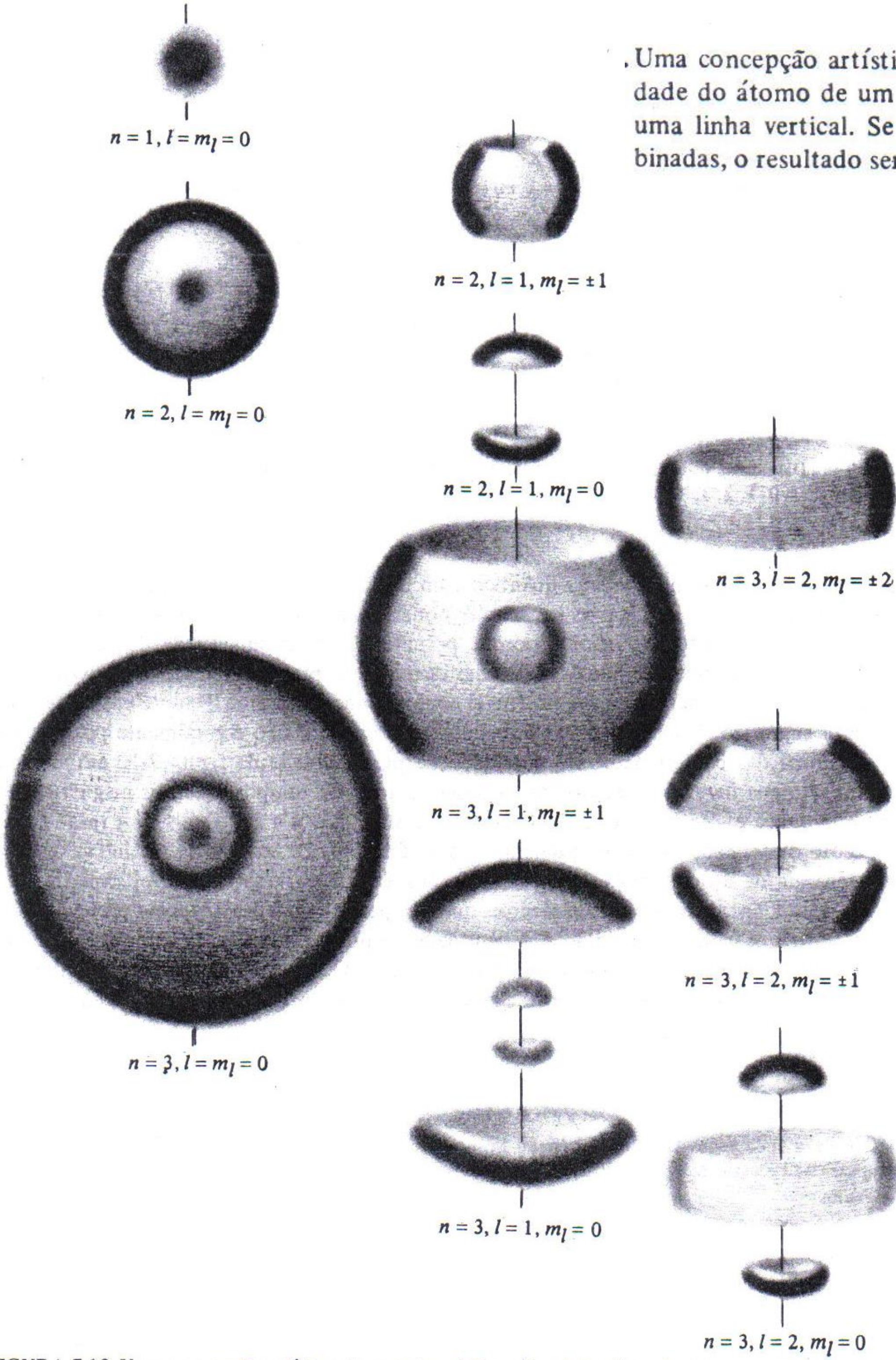
```
Plot3D[(x^2+y^2) * Exp[-(Sqrt[x^2+y^2]/3)] * (x/Sqrt[x^2+y^2]) * (y/Sqrt[x^2+y^2]),
{x,-20,20},{y,-15,15},PlotPoints→35,ViewPoint→{-1.239,-1.611,0.735}]
```


+
−
+
−
y
x
$d_{x^2-y^2}$
+
−
+
y
x
d_{z^2}
z
−
+
+
−
y
x
d_{xy}
z
−
+
−
+
y
x
d_{xz}
z
+
−
−
+
y
x
d_{yz}



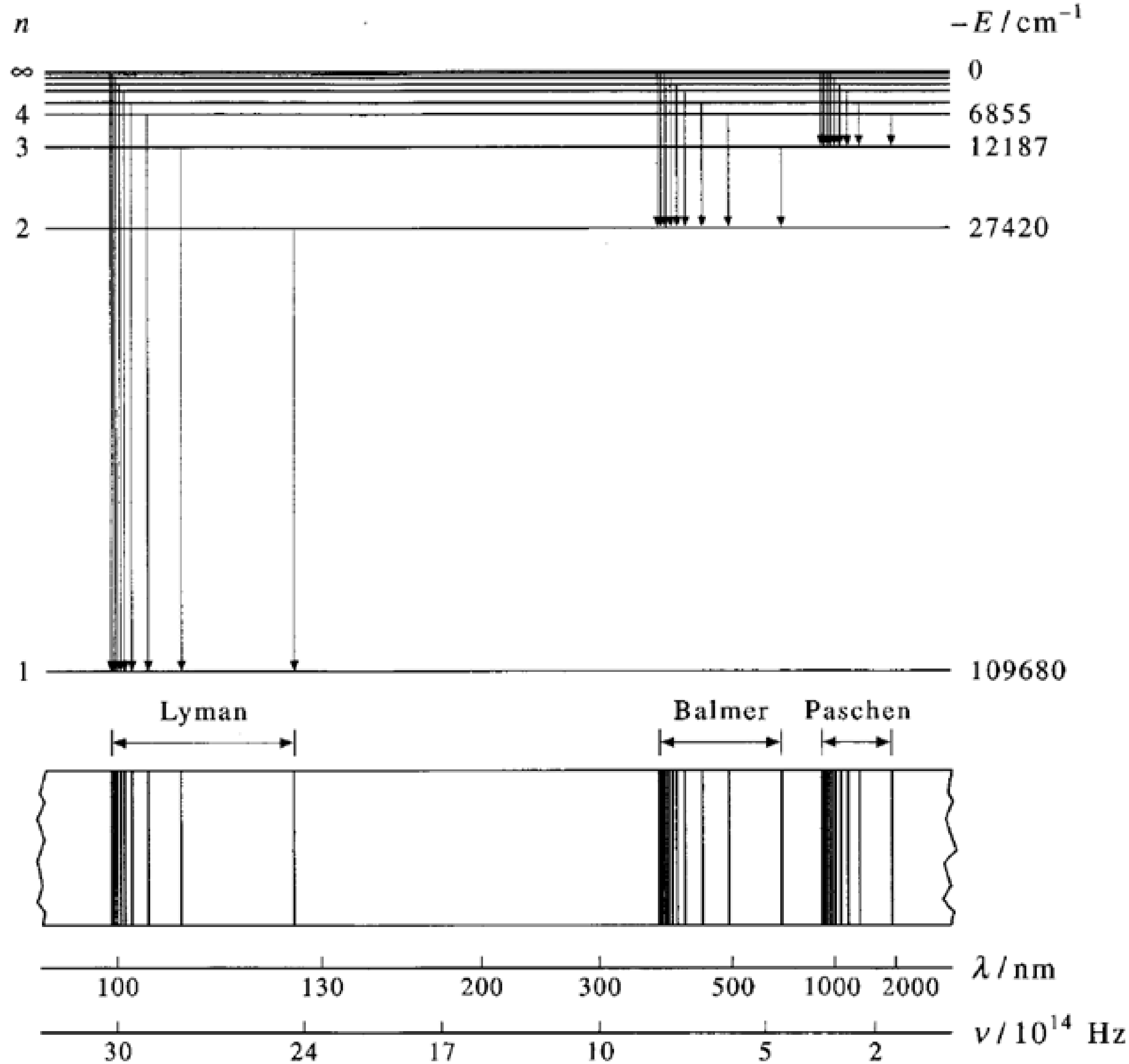
z
y
x
d_{z^2}
$d_{x^2-y^2}$
d_{xy}
d_{yz}
d_{zx}


Radial distribution function
1s orbital
r
Radial distribution function
2s orbital
2p orbital
r
Radial distribution function
3s orbital
3p orbital
3d orbital
r
The maximum value of the radial distribution function is the most probable distance from the nucleus for the electron.

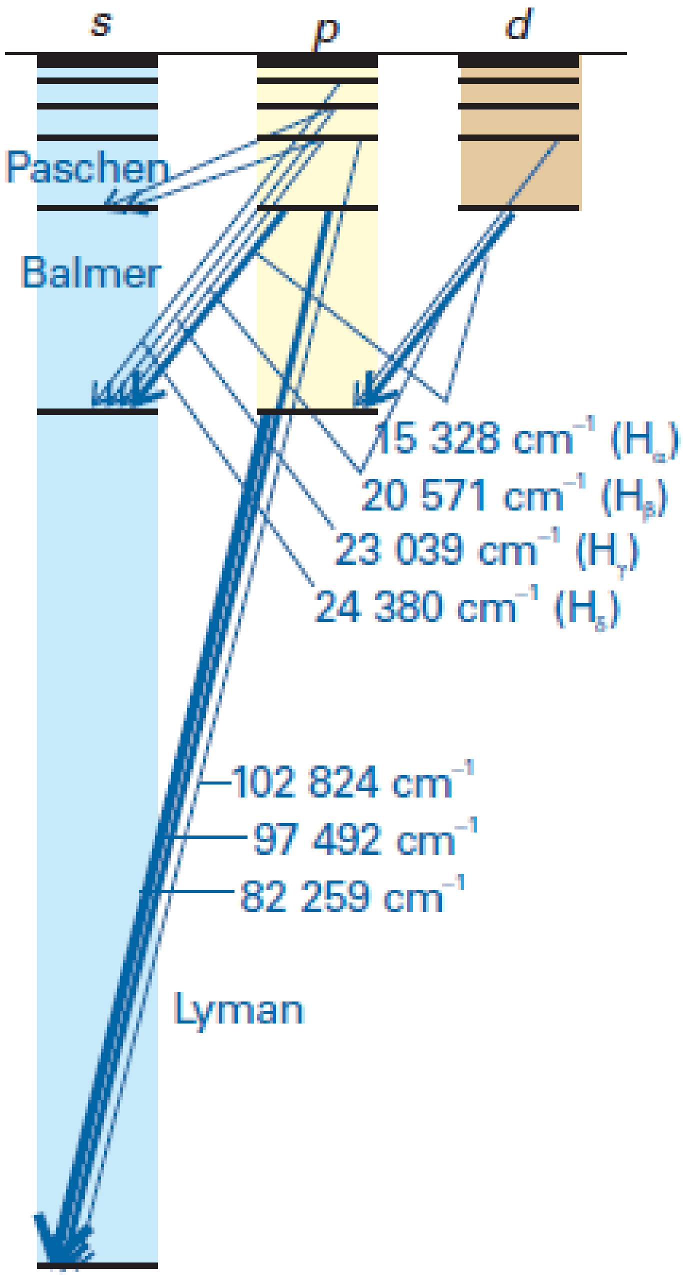


Uma concepção artística do aspecto tridimensional de várias funções densidade de probabilidade do átomo de um elétron. Para cada um dos desenhos o eixo dos z está representado por uma linha vertical. Se todas as densidades de probabilidade para um dado n e l forem combinadas, o resultado será esfericamente simétrico.

FIGURA 7.10 Uma concepção artística



n
−E / cm⁻¹
∞
0
4
6855
3
12187
2
27420
1
109680
Lyman
Balmer
Paschen
λ / nm
100
130
200
300
500
1000
2000
ν / 10¹⁴ Hz
30
24
17
10
5
2



regras de seleção

$$\Delta l = \pm 1 \qquad \Delta m_l = 0, \pm 1$$

Fig. 10.17 A Grotrian diagram that summarizes the appearance and analysis of the spectrum of atomic hydrogen. The thicker the line, the more intense the transition.