

2021.07.19

Lecture 9



서울대학교
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Department of Chemistry

PChem 2

Physical Chemistry 2

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Physical Chemistry 2

Lecture 9. The Hydrogen Atom

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Topics in Lecture 9

System with spherical symmetries

Angular momentum

Hydrogen atomic orbitals

In Atkins' *Physical Chemistry* (11th ed.),

8A Hydrogenic atoms

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Systems with spherical symmetries

In spherical coordinates, the time-independent Schrödinger equation reads

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

Start from *separation of variables*: split into *radial* part and *angular* part.

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

$$-\frac{\hbar^2}{2m} \left[\frac{Y}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \frac{R}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial Y}{\partial \theta} \right) + \frac{R}{r^2 \sin^2 \theta} \frac{\partial^2 Y}{\partial \phi^2} \right] + VRY = ERY$$

Dividing by RY and multiplying by $-2mr^2/\hbar^2$:

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

Left term only depends to r and right term only depends to angular variables. For some reasons, we will write this separation constant in the form $l(l+1)$.



Systems with spherical symmetries

Separated equations are

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

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

We already dealt with angular equation:

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

Solution of this equation is *spherical harmonics* $Y(\theta, \phi)$. Actually, spherical harmonics always emerge when you solve system with spherical symmetries. Therefore in general, our main interest is related to *radial* problems. In case of hydrogen atom, we need to solve only the radial equation.

$$Y_l^m(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-|m|)!}{(l+|m|)!}} P_l^{|m|}(\cos \theta) e^{im\phi} \quad \text{where } l = 0, 1, 2, \dots \text{ and } m = 0, \pm 1, \dots, \pm l$$

Spherical harmonics

Note that conditions for l and m are identical to the quantum numbers of hydrogen atoms. Also, spherical harmonics form an orthonormal set.

$$\int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi Y_l^m(\theta, \phi)^* Y_n^k(\theta, \phi) = \delta_{ln} \delta_{mk}$$

Or, with Dirac notation,

$$\langle l, m | n, k \rangle = \delta_{ln} \delta_{mk}$$

Before we deal with the radial wavefunction, we need to discuss very important angular dynamic variable: the angular momentum.

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Angular momentum

QM operator corresponding to the square of angular momentum is

$$\hat{L}^2 = -\hbar^2 \left[\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right] \quad (\text{from } \hat{H} = \frac{\hat{L}^2}{2I})$$

Therefore, spherical harmonics are eigenfunctions of \hat{L}^2 , consequently.

$$\hat{L}^2 Y_l^m(\theta, \phi) = \hbar^2 l(l+1) Y_l^m(\theta, \phi)$$

So quantum-mechanical angular momentum is

$$|L| = \hbar \sqrt{l(l+1)} \quad (l = 0, 1, 2, \dots)$$

The quantum number l , originated from the spherical harmonics, is called *angular momentum quantum number*.

Angular momentum

Spherical harmonics version of angular momentum:

$$\hat{L}_x = -i\hbar \left(-\sin\phi \frac{\partial}{\partial\theta} - \cot\theta \cos\phi \frac{\partial}{\partial\phi} \right)$$

$$\hat{L}_y = -i\hbar \left(\cos\phi \frac{\partial}{\partial\theta} - \cot\theta \sin\phi \frac{\partial}{\partial\phi} \right)$$

$$\hat{L}_z = -i\hbar \frac{\partial}{\partial\phi}$$

By substitution, we can check that spherical harmonics are eigenfunctions of \hat{L}_z .

$$\hat{L}_z e^{im\phi} = \hbar m e^{im\phi} \implies \hat{L}_z Y_l^m(\theta, \phi) = \hbar m Y_l^m(\theta, \phi)$$

$$L_z = m\hbar, m = 0, \pm 1, \dots, \pm l$$

The quantum number m is called *magnetic quantum number*.

Note that \hbar is a fundamental measure of the angular momentum of a QM system.

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Angular momentum

Restriction for m is from the simple identity.

$$\begin{aligned}\hat{L}^2 Y_l^m &= \hbar^2 l(l+1) Y_l^m, \quad \hat{L}_z^2 Y_l^m = \hbar^2 m^2 Y_l^m \\ (\hat{L}^2 - \hat{L}_z^2) Y_l^m &= [l(l+1) - m^2] \hbar^2 Y_l^m = (\hat{L}_x^2 + \hat{L}_y^2) Y_l^m \geq 0 \\ [l(l+1) - m^2] \hbar^2 &\geq 0, \quad |m| \leq l\end{aligned}$$

Naming for m is related to splitting of hydrogen spectrum lines under applied magnetic field.

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Angular momentum

We can measure \hat{L}^2 and \hat{L}_z simultaneously: i.e., they commute.

However, \hat{L}_x and \hat{L}_y does not commute with each other: we cannot measure \hat{L}_x and \hat{L}_y simultaneously, with infinite accuracy.



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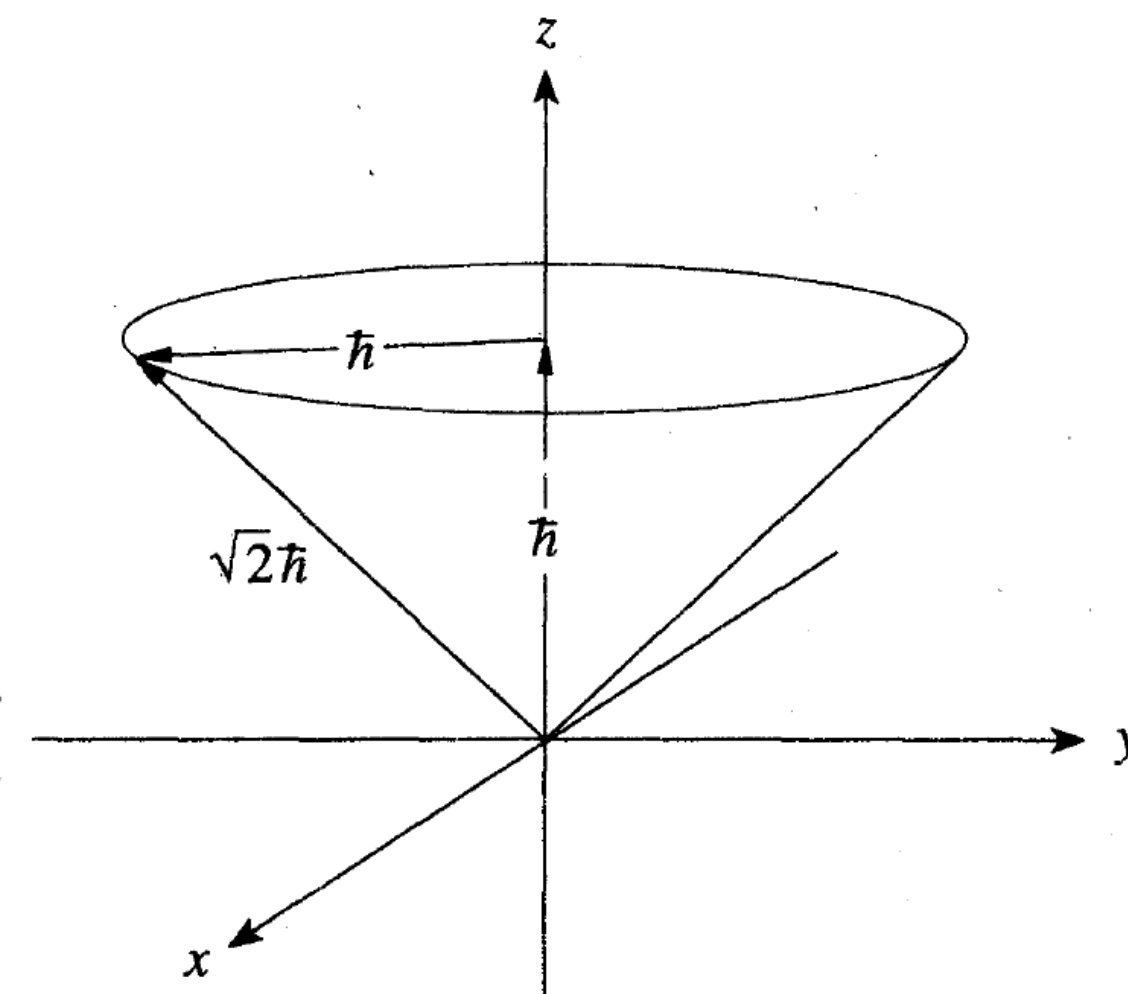


FIGURE 6.1

The $m = +1$ component of the angular-momentum state $l = 1$. The angular momentum describes a cone because the x and y components cannot be specified. The projection of the motion onto the x - y plane is a circle of radius \hbar centered at the origin (Example 6–8).

Radial equation

The form of radial equation is

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

We will not solve this equation in detail, but accommodate the result.

The quantized energy, E_n is

$$E_n = -\frac{me^4}{8\epsilon_0^2 \hbar^2 n^2} = -\frac{me^4}{32\pi^2 \epsilon_0^2 \hbar^2 n^2} = -\frac{e^2}{8\pi\epsilon_0 a_0 n^2} \quad (n = 1, 2, \dots)$$

In the course of solving equation, we find not only that an integer n occurs naturally, but that n must satisfy the condition

$$0 \leq l \leq n - 1$$

We call n *principal quantum number*.

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Radial equation

The solutions to the equation depends on two quantum numbers, n and l .

$$R_{nl}(r) = - \left\{ \frac{(n-l-1)!}{2n[(n+l)!]^3} \right\}^{1/2} \left(\frac{2}{na_0} \right)^{l+3/2} r^l e^{-r/na_0} L_{n+l}^{2l+1} \left(\frac{2r}{na_0} \right)$$

where the L_{n+l}^{2l+1} are called *associated Laguerre polynomials*.

TABLE 6.4

The first few associated Laguerre polynomials.

$n = 1,$	$l = 0$	$L_1^1(x) = -1$
$n = 2,$	$l = 0$	$L_2^1(x) = -2!(2 - x)$
	$l = 1$	$L_3^3(x) = -3!$
$n = 3,$	$l = 0$	$L_3^1(x) = -3!(3 - 3x + \frac{1}{2}x^2)$
	$l = 1$	$L_4^3(x) = -4!(4 - x)$
	$l = 2$	$L_5^5(x) = -5!$
$n = 4,$	$l = 0$	$L_4^1(x) = -4!(4 - 6x + 2x^2 - \frac{1}{6}x^3)$
	$l = 1$	$L_5^3(x) = -5!(10 - 5x + \frac{1}{2}x^2)$
	$l = 2$	$L_6^5(x) = -6!(6 - x)$
	$l = 3$	$L_7^7(x) = -7!$



Hydrogen atomic orbitals

The complete hydrogen atomic wavefunctions are

$$\psi_{nlm} = R_{nl}(r)Y_l^m(\theta, \phi) = \sqrt{\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-r/na_0} \left(\frac{2r}{na_0}\right)^l L_{n-l-1}^{2l+1}(2r/na_0) Y_l^m(\theta, \phi)$$

(Retrieved from Grrifiths QM: **warning** notation for associated Laguerre polynomial is different here)

TABLE 6.5

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.

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



Hydrogen atomic orbitals

Principal quantum number ($n = 1, 2, 3, \dots$)

The energy of the hydrogen atom depends upon only the principal quantum number. Determines the size of orbital and the number of nodes.

Angular momentum quantum number ($l = 0, 1, \dots, n - 1$)

$l = 0, 1, 2, 3, \dots$ corresponds to s, p, d, f, ...

The angular momentum of the electron about the proton is determined completely by l .

Magnetic quantum number ($|m| \leq l$)

The z component of angular momentum is determined completely by m .

In the absence of a magnetic field, each energy level has a degeneracy of $2l+1$.

Related to *Zeeman effect*.

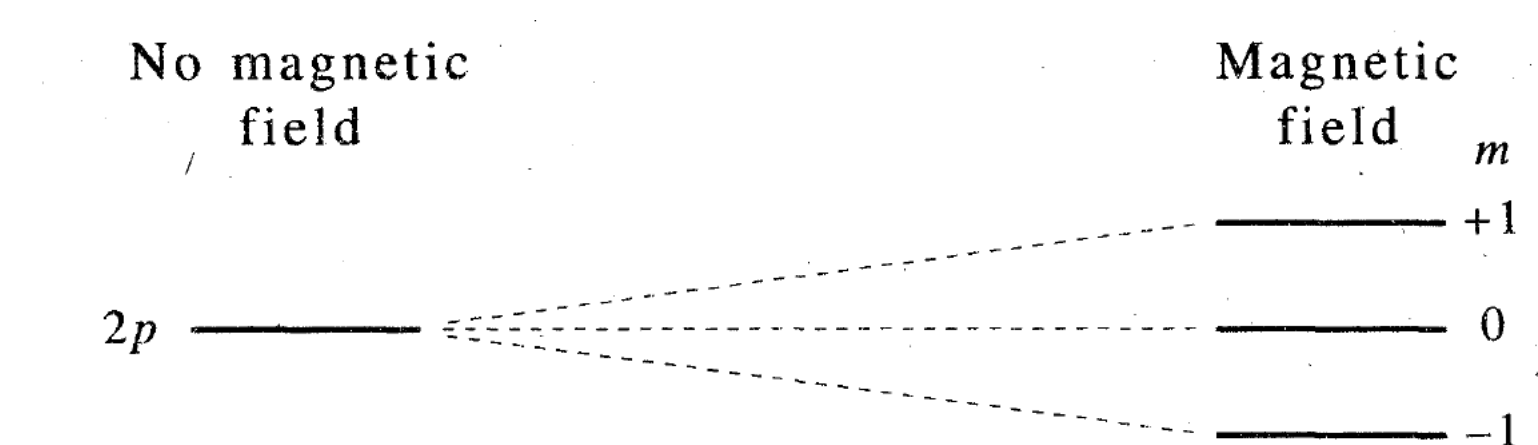
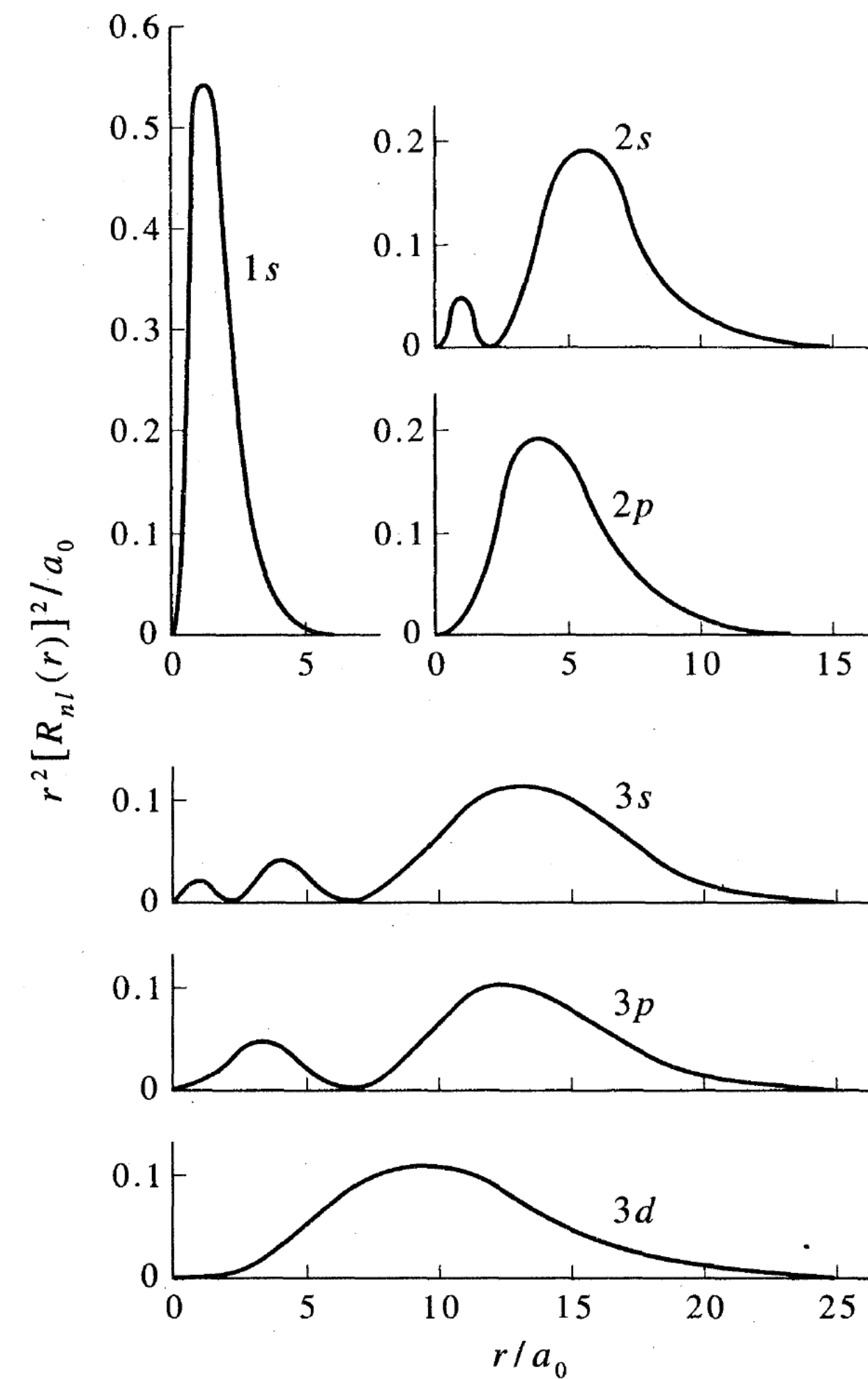


FIGURE 6.2

The splitting of the $2p$ state of a hydrogen atom in a magnetic field.

Hydrogen atomic orbitals



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p orbitals

When $l \neq 0$, wavefunctions depend on angles: not spherically symmetric wavefunctions!

For $l = 1$ case, possible m values are $m = -1, 0, 1$. So, there are three p orbitals for each n . The simplest of these spherical harmonics is

$$Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

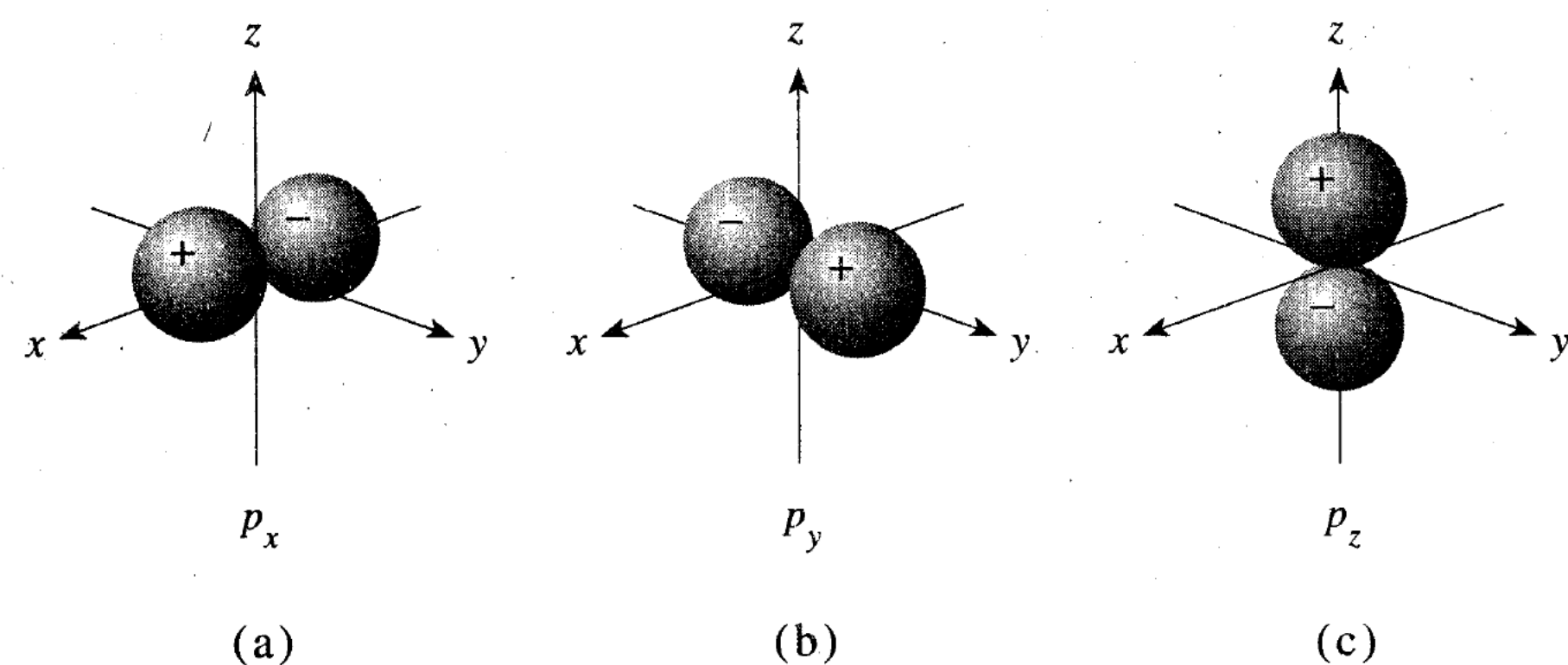


FIGURE 6.4

Three-dimensional polar plots of the angular part of the real representation of the hydrogen atomic wave functions for $l = 1$ (see Equations 6.62 for real representations of p_x and p_y .)



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p orbitals

However, for $m \neq 0$ case, angular functions are more difficult to represent pictorially. They not only depend on ϕ but also are complex functions. Since following two spherical harmonics correspond to the same energy, we usually use *linear combination* of them, to eliminate complex terms.

$$Y_1^{\pm 1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin \theta e^{\pm i\phi}$$

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

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

$l = 1, m = 0$ term remains as p_z orbital.

$$p_z = Y_1^0(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$





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d orbitals

d orbitals also suffer similar linear combination.

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

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

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

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

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

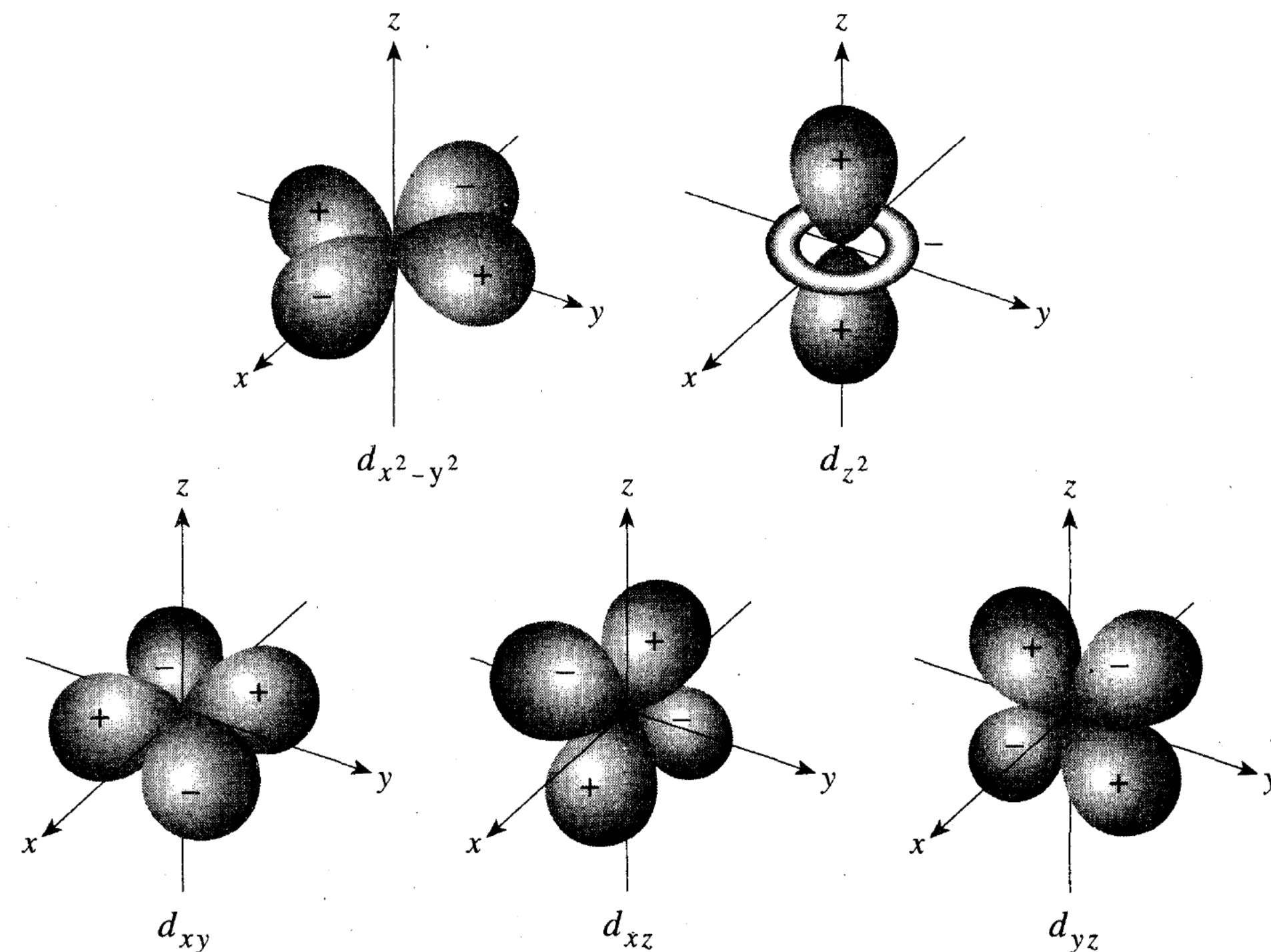


FIGURE 6.7

Three-dimensional plots of the angular part of the real representation of the hydrogen atomic wave functions for $l = 2$. Such plots show the directional character of these orbitals but are not good representations of the shape of these orbitals because the radial functions are not included.

Hydrogen atomic orbitals

TABLE 6.6

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.

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

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Hydrogen atomic orbitals

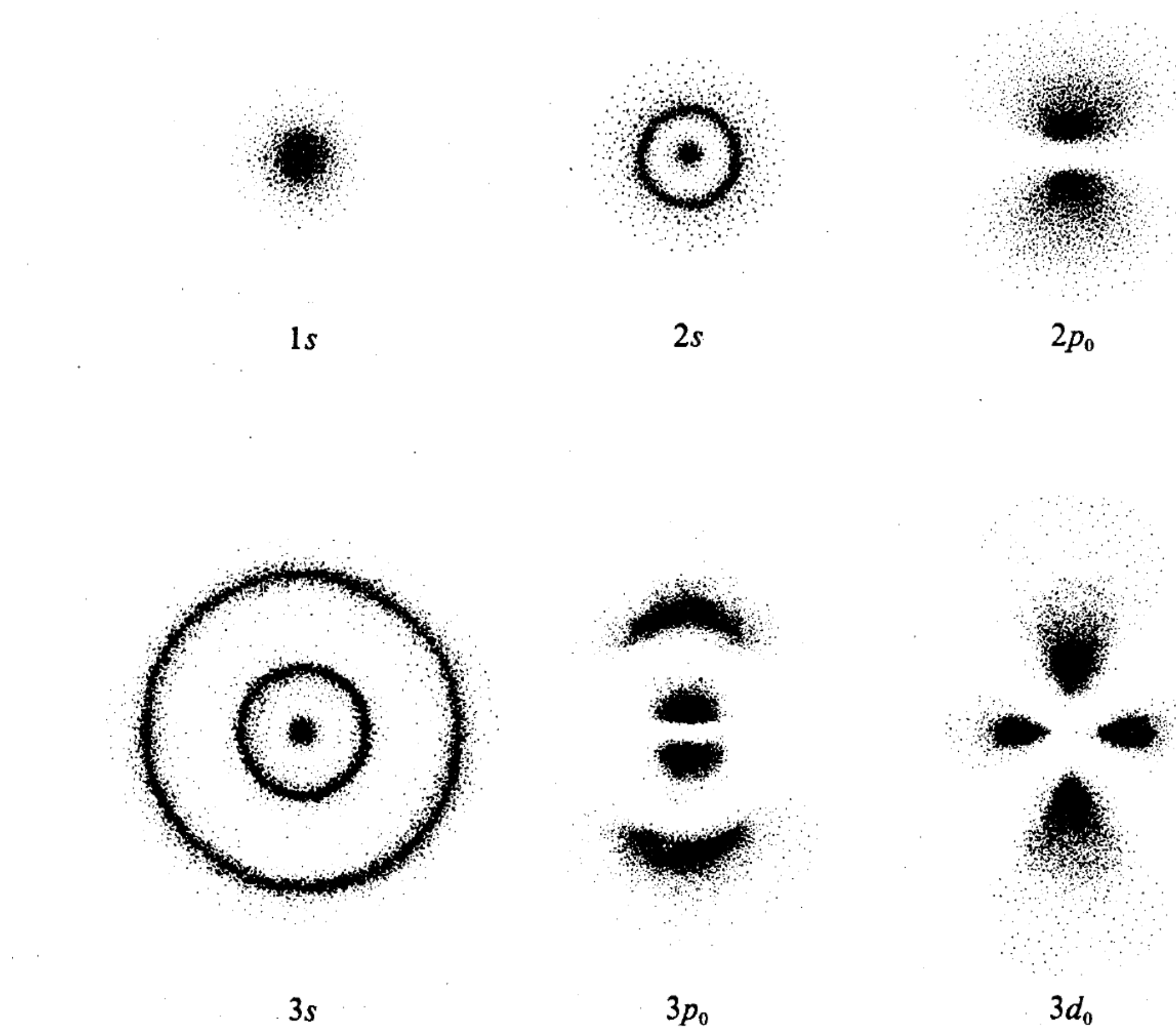


FIGURE 6.5

Probability density plots of some hydrogen atomic orbitals. The density of the dots is proportional to the probability of finding the electron in that region.

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