The atom I

Let's now tackle an especially relevant problem in quantum mechanics: the solution of electron orbitals! (Chapter 8 of Serway).

- We expect to have some constants of motion:
  1. Total kinetic energy: quantum number is n
  2. Total angular momentum L: quantum number is ℓ
  3. Projection of L onto one axis: quantum number is m_ℓ
- The time-independent Schrödinger equation in multiple dimensions involves a Laplacian ∇^2:

$$\frac{-\hbar^2}{2m}\nabla^2\psi + U(r)\psi = E\psi$$

- We'll use spherical coordinates (r, θ, ϕ), where θ is angle from the $\hat{z}$ axis, while ϕ is the azimuthal angle. The Laplacian or second derivative ∇^2 in spherical coordinates (r, θ, ϕ) becomes (equivalent but different form from Serway)

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

The atom II

Assume separable variables, as we did with the 2D infinite well (Serway Eq. 8.11):

$$\psi(r,\theta,\phi) = R(r)\Theta(\theta)\Phi(\phi)$$

The Schrödinger equation then becomes

$$\frac{-\hbar^2}{2m}\left\{\frac{\Theta\Phi}{r^2}\frac{\partial}{\partial r}(r^2\frac{\partial R}{\partial r}) + \frac{R}{r^2}\left[\frac{\Phi}{\sin(\theta)}\frac{\partial}{\partial\theta}(\sin(\theta)\frac{\partial\Theta}{\partial\theta}) + \frac{\Theta}{\sin^2(\theta)}\frac{\partial^2\Phi}{\partial\phi^2}\right]\right\} + U(r)R\Theta\Phi = ER\Theta\Phi$$

Multiply through by $\frac{-2m}{\hbar^2}\frac{r^2\sin^2(\theta)}{R\Theta\Phi}$ and rearrange. Gives (see Serway Eq. 8.12)

(1) $$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \frac{2m}{\hbar^2}r^2\sin^2(\theta)(U(r)-E) - \frac{\sin^2(\theta)}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin(\theta)}{\Theta}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right).$$

Look at this result: the left hand side depends on $\Phi(\phi)$, while the right hand side does not. This must be true for any (r,θ) so the left hand side equals a constant!

The atom III

Again, we have

(2) $$\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = \text{constant} \qquad \text{or} \qquad \frac{d^2\Phi}{d\phi^2} - (\text{constant})\Phi = 0$$

Let's assume this is associated with the angular momentum projected on the $\hat{z}$ axis of L_z involving the quantum number m_ℓ. In this case we can assume solutions to (see Serway Eq. 8.13)

(3) $$\frac{d^2\Phi}{d\phi^2} + m_\ell^2\Phi = 0$$

which have the form

(4) $$\Phi(\phi) = \frac{1}{\sqrt{2\pi}}e^{im_\ell\phi}$$

The $1/\sqrt{2\pi}$ term gives us the proper normalization of $\int_0^{2\pi} |\Phi(\phi)|^2\, d\phi = 1$. Note also that $\Phi(\phi)$ has the same value at ϕ as it does at $\phi + 2n\pi$: no matter how many times we go around the circle, the wave at the same place should be the same. This is another way of saying that m_ℓ has to be an integer.

The atom IV

From Eq. 7 of $\frac{d^2\Phi}{d\phi^2} + m_\ell^2\Phi = 0$, we can say that $\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -m_\ell^2$, so we can substitute $-m_\ell^2$ on the left hand side of Eq. 1:

$$(5)\quad -m_\ell^2 = \frac{2m}{\hbar^2}r^2\sin^2(\theta)(U(r)-E) - \frac{\sin^2(\theta)}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{\sin(\theta)}{\Theta}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right).$$

This can be rearranged to give (see Serway Eq. 8.14)

$$(6)\quad \frac{1}{\Theta\sin(\theta)}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) - \frac{m_\ell^2}{\sin^2(\theta)} = \frac{2m}{\hbar^2}r^2(U(r)-E) - \frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right).$$

Again, we have all dependency on $\Theta(\theta)$ on the left, and all dependency on $R(r)$ on the right. We must satisfy this for any r and any θ, so both sides must equal a constant. With some foresight, let's call this constant $-\ell(\ell+1)$.

The atom V

With both the right and left hands sides of Eq. 6 equal to $-\ell(\ell+1)$, we now obtain separate differential equations in r and in θ. The θ equation is like Serway Eq. 8.15

$$\frac{1}{\sin(\theta)}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right)+\left[\ell(\ell+1)-\frac{m_\ell^2}{\sin^2(\theta)}\right]\Theta=0 \tag{7}$$

and the r equation is like Serway Eq. 8.17:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2m}{\hbar^2}\left[(E-U(r))-\frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]R=0 \tag{8}$$

Now recall for a Coulomb force we have $E-U(r)=-\frac{1}{4\pi\epsilon_0}\frac{Ze^2}{r}$ so Eq. 8 becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)-\frac{2m}{\hbar^2}\left[\frac{Ze^2}{4\pi\epsilon_0 r}+\frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]R=0 \tag{9}$$

where m is the reduced mass $m_r=\frac{m_e M}{m_e+M}$ as before. Mathematically similar to drum head modes, electrostatics on spheres, *etc.*

Radial wavefunctions I

Consider again the radial differential equation:

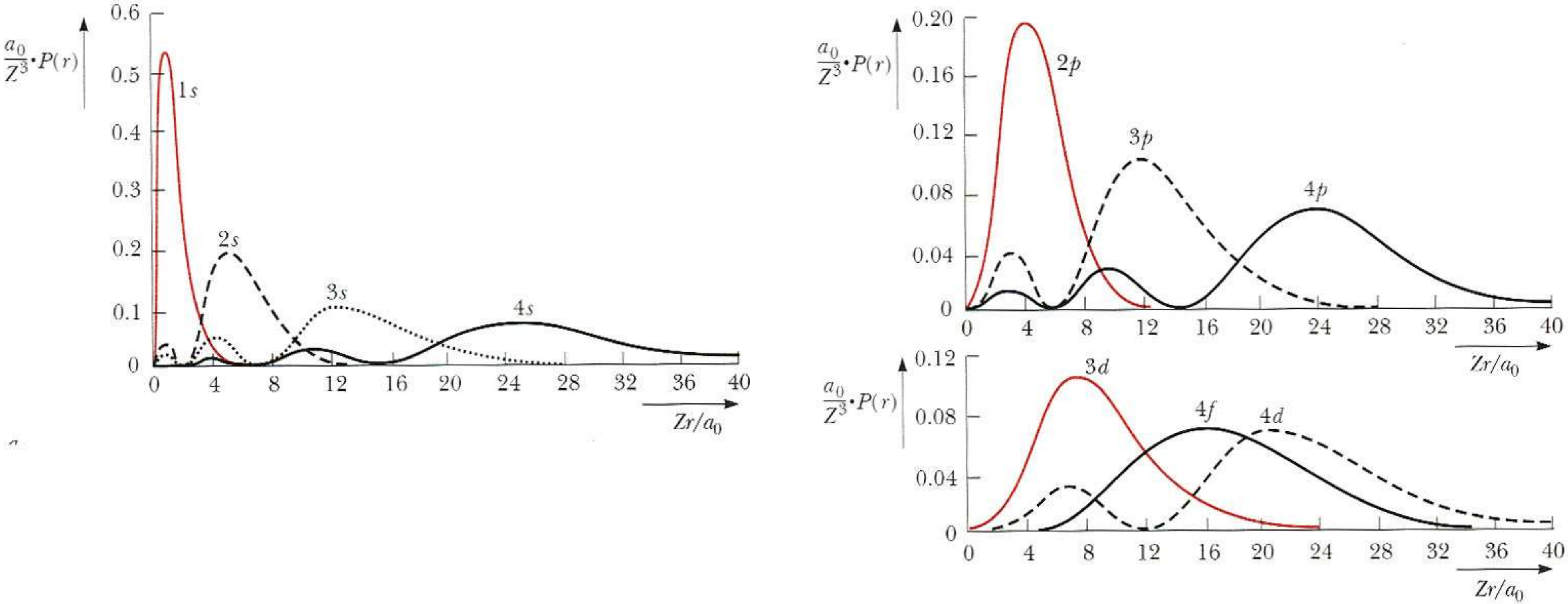
$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) - \frac{2m}{\hbar^2}\left[\frac{Ze^2}{4\pi\epsilon_0 r} + \frac{\hbar^2}{2mr^2}\ell(\ell+1)\right]R = 0$$

It's beyond our course to derive the solutions, but they have the form $R_{n\ell}(r)$ with normalization $\int_0^\infty R_{n\ell}^2(r)\, r^2\, dr = 1$. The first several solutions, expressed in terms of the Bohr radius $a_0 = (4\pi\epsilon_0\hbar^2)/(m_e e^2) = 0.053$ nm, are (see Serway Table 8.4):

$$R_{10}(r) = \left(\frac{Z}{a_0}\right)^{3/2} 2e^{-Zr/a_0}$$
$$R_{20}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \left(2 - \frac{Zr}{a_0}\right) e^{-Zr/2a_0}$$
$$R_{21}(r) = \left(\frac{Z}{2a_0}\right)^{3/2} \frac{Zr}{\sqrt{3}a_0} e^{-Zr/2a_0}$$
$$R_{30}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} 2\left[1 - \frac{2Zr}{3a_0} + \frac{2}{27}\left(\frac{Zr}{a_0}\right)^2\right] e^{-Zr/3a_0}$$
$$R_{31}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{4\sqrt{2}}{3}\frac{Zr}{a_0}\left(1 - \frac{1}{6}\frac{Zr}{a_0}\right) e^{-Zr/3a_0}$$
$$R_{32}(r) = \left(\frac{Z}{3a_0}\right)^{3/2} \frac{2}{27}\sqrt{\frac{2}{5}}\left(\frac{Zr}{a_0}\right)^2 e^{-Zr/3a_0}$$

Radial wavefunctions II

We can calculate the probability of being in a region $r_1 \leq r \leq r_2$ from $\int_{r_1}^{r_2} R_{n\ell}^2(r)\, r^2\, dr$. Here are several of the radial probability distribution functions $r^2 R_{n\ell}(r)$ (Serway Fig. 8.11):



Interpretation of n and ℓ

n: principal quantum number, which determines the energy

ℓ: orbital quantum number, or angular momentum quantum number

The notation of "shells" comes from Moseley's x-ray work, before Bohr.

n	shell
1	K
2	L
3	M
4	N
5	O
6	P

ℓ	symbol
0	s for *sharp*
1	p for *principal*
2	d for *diffuse*
3	f for *fundamental*
4	g
5	h

One typically speaks of a $1s$ state rather than a 10, $K0$, or Ks state.

Spherical harmonics I

We had in Eq. 7 an azimuthal differential equation (see Serway Eq. 8.15):

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

This can be solved in terms of Legendre polynomials (see Serway Table 8.2). It is more common to talk about the product $\Phi(\phi)\Theta(\theta)$ as *spherical harmonics* or $Y_\ell^{m_\ell}(\theta,\phi)$. They occur in many situations in physics, and thus were already known to early researchers in quantum mechanics. The first several normalized spherical harmonics are (see Serway Table 8.3)

$$\begin{aligned} Y_0^0 &= \tfrac{1}{\sqrt{4\pi}} & Y_1^0 &= \sqrt{\tfrac{3}{4\pi}}\cos\theta \\ Y_1^1 &= -\sqrt{\tfrac{3}{8\pi}}\sin\theta\, e^{i\phi} & Y_2^0 &= \sqrt{\tfrac{5}{4\pi}}(\tfrac{3}{2}\cos^2\theta - \tfrac{1}{2}) \\ Y_2^1 &= -\sqrt{\tfrac{15}{8\pi}}\sin\theta\,\cos\theta\, e^{i\phi} & Y_2^2 &= \tfrac{1}{4}\sqrt{\tfrac{15}{2\pi}}\sin^2\theta\, e^{2i\phi} \end{aligned}$$

Allowed values for ℓ are $\ell = 0, 1, \ldots, (n-1)$. Allowed values for m_ℓ are $m_\ell = -\ell, (-\ell+1), \ldots, 0, \ldots, (\ell-1), \ell$.

Spherical harmonics II

- Spherical harmonics $Y_\ell^{m_\ell}(\theta, \phi)$ show up lots of times in physics, such as in the motion of drum heads, electromagnetic modes in cylinders and spheres, and so on.
- It turns out that the spherical harmonics for an orthonormal basis set, so that one can express any function $f(\theta, \phi)$ in terms of some linear combination of spherical harmonics $Y_\ell^{m_\ell}(\theta, \phi)$.
- Because they are orthogonal, their overlap is driven by how they are integrated over a spherical coordinate system:

$$\int Y_{\ell_f}^{m_{\ell,f}}(\theta, \phi)\, Y_{\ell_i}^{m_{\ell,i}}(\theta, \phi)\, \sin\theta \, d\theta \, d\phi$$

  It turns out that the integral is zero unless $|\ell_f - \ell_i| = 1$ or $\Delta\ell = \pm 1$ (Serway Eq. 8.40). This means that only certain electronic transitions are allowed!
- In fact this is weakly violated in multielectron atoms because the wave function of one electron is slightly modified by the presence of other electrons, giving slight mixing of spherical harmonics—but $\Delta\ell = \pm 1$ is still a pretty good rule.

Selection rules

Here's an illustration from Serway on how the $\Delta\ell = \pm1$ selection rule can play out:

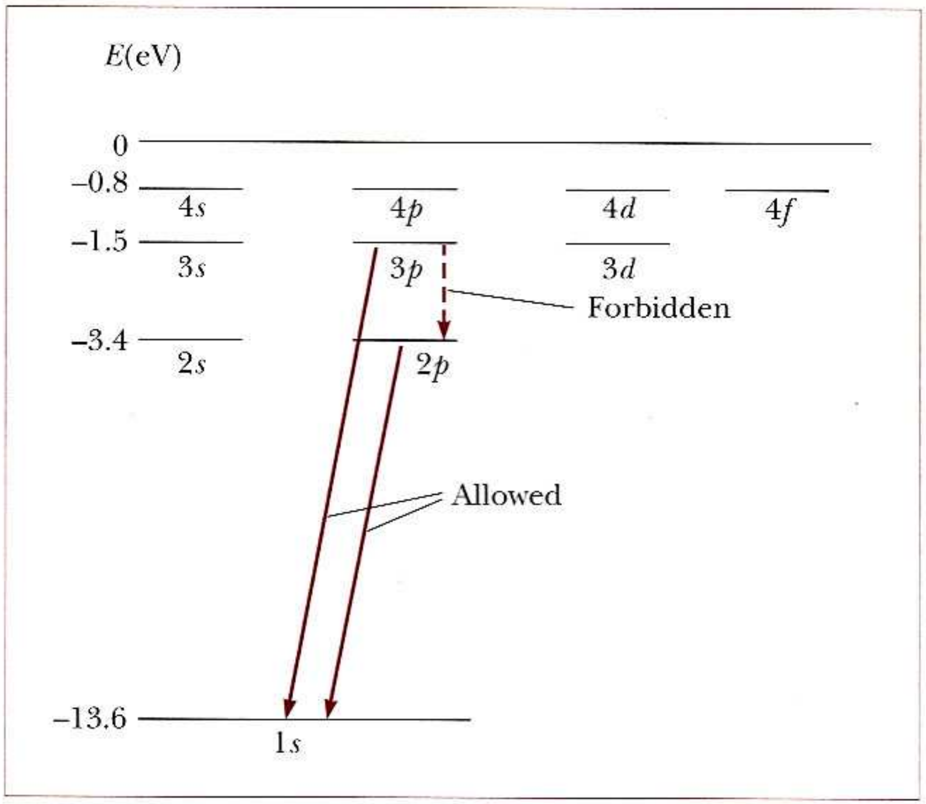


Figure 8.8 Energy-level diagram of atomic hydrogen. Allowed photon transitions are those obeying the selection rule $\Delta\ell = \pm1$. The $3p \rightarrow 2p$ transition ($\Delta\ell = 0$) is said to be forbidden, though it may still occur (but only rarely).

Putting it all together

- Recall that we assumed a wavefunction solution in separable variables:

$$\psi(r,\theta,\phi) = R_{n,\ell}(r)\Theta_{\ell,m_\ell}(\theta)\Phi_{m_\ell}(\phi)$$

$$\psi_{n,\ell,m_\ell}(r,\theta,\phi) = R_{n,\ell}(r)\,Y_\ell^{m_\ell}(\theta,\phi) \tag{10}$$

  We now have a full solution to the time-independent Schrödinger equation for electrons in an atom!

- We can plug these wavefunctions into the Schrödinger equation and calculate the energy. Lo and behold, to first approximation we get a simple and familiar result, just like Bohr obtained:

$$E_n = -E_0\frac{Z^2}{n^2} \tag{11}$$

- But the wavefunctions are not limited to a few discrete radii! Instead, they are fuzzy in both radius and in angle! Boy, was Bohr lucky that his wrong picture gave so many right answers!

Pictures of wavefunctions

To look at the probability distribution for an electron in a particular state ψ_{n,ℓ,m_ℓ}, we need to consider the integral in spherical coordinates:

$$\int_{r=0}^{\infty} \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} |\psi_{n,\ell,m_\ell}(r,\theta,\phi)|^2 \, r^2 \, dr \, \sin\theta \, d\theta \, d\phi = 1$$

Considering that the spherical harmonic $Y_\ell^{m_\ell}$ parts of ψ_{n,ℓ,m_ℓ} come pre-normalized, the relative probability of being at a particular radius r is given by (Serway Eq. 8.44)

$$P(r)\, dr = |\psi|^2 \, 4\pi r^2 \, dr = r^2 |R_{n,\ell}(r)|^2 \, dr$$

We can therefore look at $r^2 R^2(r)$ to see more of what the electron wavefunctions look like.

Electron wavefunctions I

Here's one picture, from T.R. Sandin, *Essentials of Modern Physics*:

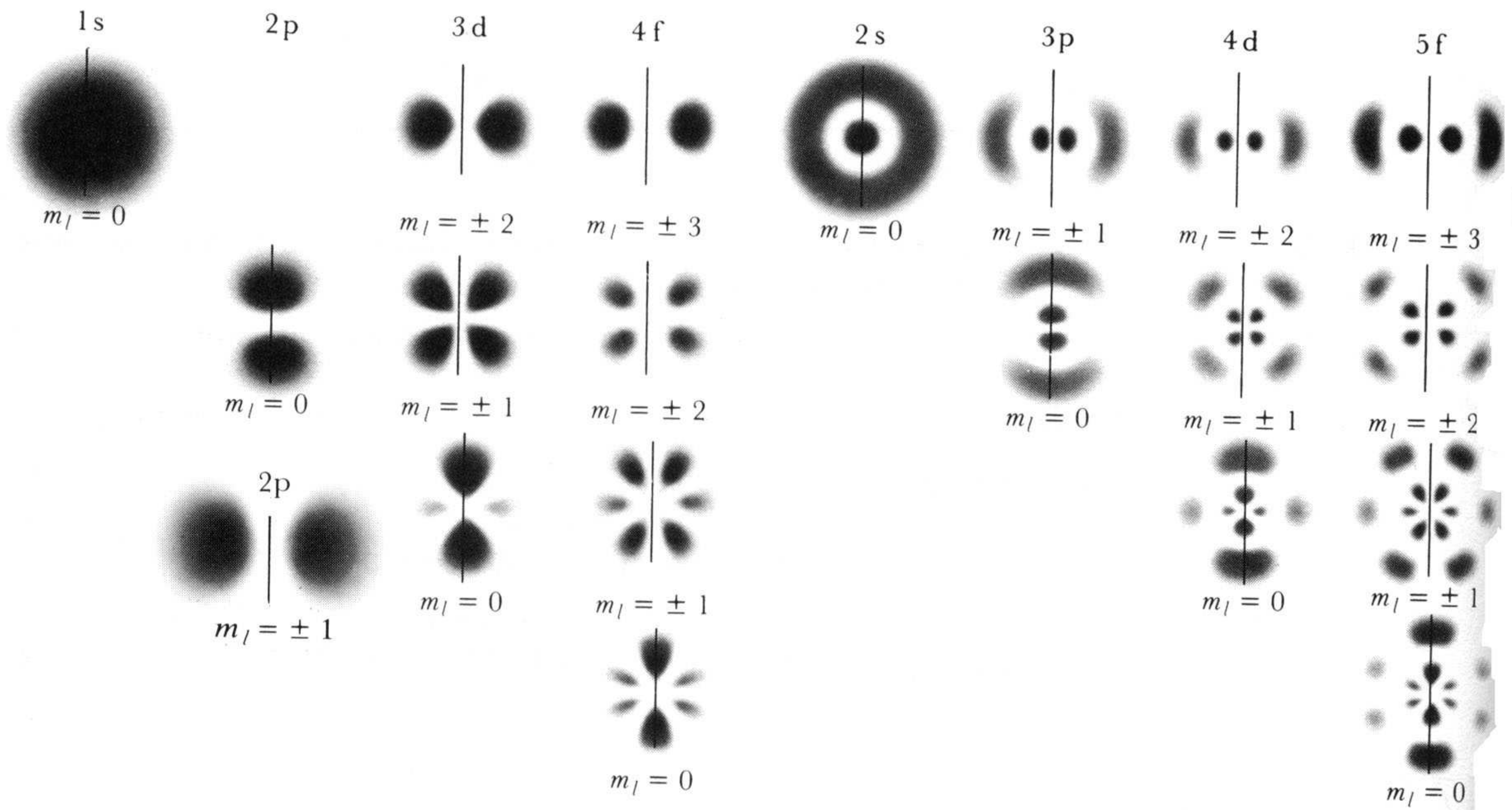


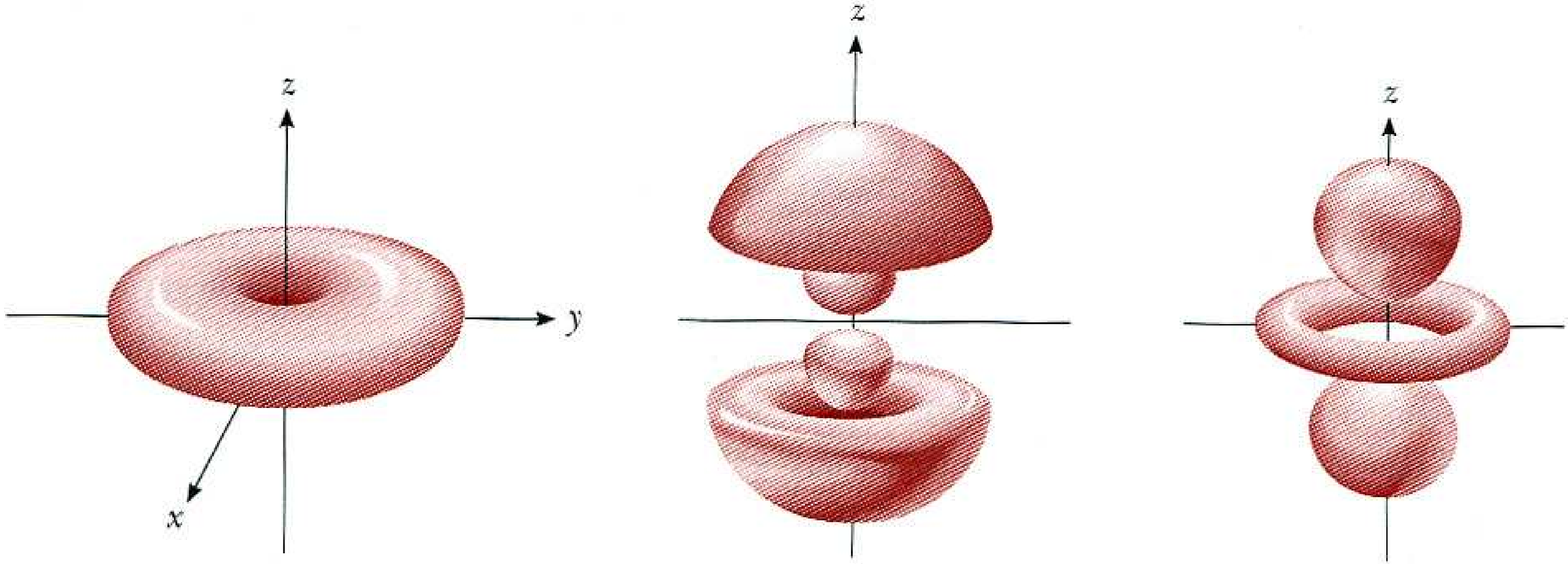
FIGURE 17.1

A photographic representation of the electron probability density, $\psi^*\psi$, for some hydrogen-like states. These are views sectioned along any plane containing the z axis but are not to scale.

Source: Courtesy of Robert B. Leighton, California Institute of Technology.

Electron wavefunctions II

Here are some "isosurface" representations, where a surface is placed at a particular probability level:



$n = 2,\ \ell = 1,\ m_\ell = \pm 1$ (a) $n = 3,\ \ell = 1,\ m_\ell = 0$ (b) $n = 3,\ \ell = 2,\ m_\ell = 0$ (c)

Figure 8.12 (a) The probability density $|\psi_{211}|^2$ for a hydrogen-like $2p$ state. Note the axial symmetry about the z-axis. (b) and (c) The probability densities $|\psi(\mathbf{r})|^2$ for several other hydrogen-like states. The electron "cloud" is axially symmetric about the z-axis for all the hydrogen-like states $\psi_{n\ell m_\ell}(\mathbf{r})$.

Electron wavefunctions III

Some more isosurface representations:

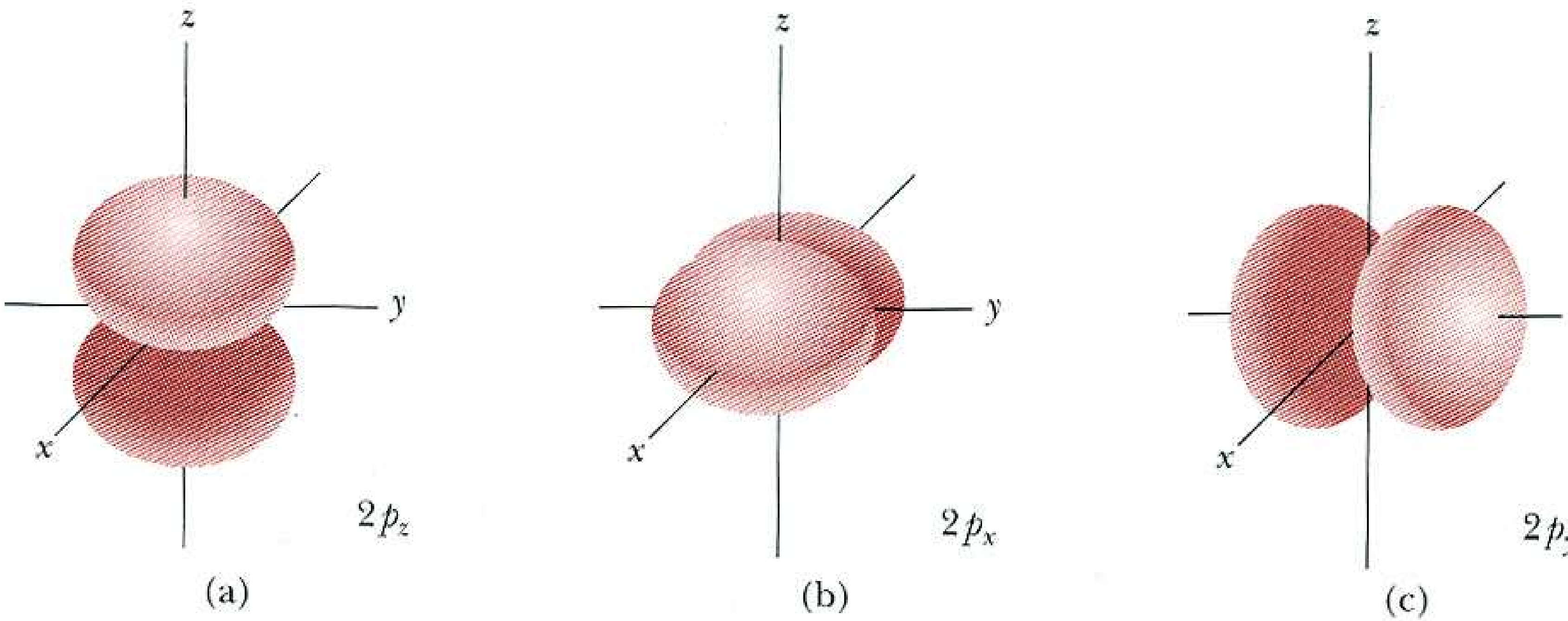


Figure 8.13 (a) Probability distribution for an electron in the hydrogenlike $2p_z$ state, described by the quantum numbers $n = 2$, $\ell = 1$, $m_\ell = 0$. (b) and (c) Probability distributions for the $2p_x$ and $2p_y$ states. The three distributions $2p_x$, $2p_y$, and $2p_z$ have the same structure, but differ in their spatial orientation.