Part IV

Multiple Dimensions: Going 3D with Quantum Physics

The 5th Wave   By Rich Tennant

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MATH DEPT RM 201

Dang kids in the Physics Department, messin' with old Mitch's flashlight again!

In this part . . .

The previous parts deal mostly with particles in one-dimensional systems. This part expands that coverage to three dimensions, like in the real world. You see how to handle quantum physics in three-dimensional coordinates — whether rectangular or spherical — which lays the groundwork for working with electrons in atoms.

Chapter 7

Rectangular Coordinates: Solving Problems in Three Dimensions

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In This Chapter

▶ Exploring the Schrödinger equation in the *x, y,* and *z* dimensions

▶ Working with free particles in 3D

▶ Getting into rectangular potentials

▶ Seeing harmonic oscillators in 3D space

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*O*ne-dimensional problems are all very well and good, but the real world has three dimensions. This chapter is all about leaving one-dimensional potentials behind and starting to take a look at spinless quantum mechanical particles in three dimensions.

Here, you work with three dimensions in rectangular coordinates, starting with a look at the Schrödinger equation in glorious, real-life 3D. You then delve into free particles, box potentials, and harmonic oscillators. ***Note:*** By the way, the next chapter uses spherical coordinates because some problems are better in one system than the other. Problems with spherical symmetry are best handled in spherical coordinates, for example.

The Schrödinger Equation: Now in 3D!

In one dimension, the time-dependent Schrödinger equation (of the type in Chapters 3 and 4 that let you find the wave function) looks like this:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x,t) + V(x,t)\psi(x,t) = i\hbar\frac{\partial}{\partial t}\psi(x,t)$$

And you can generalize that into three dimensions like this:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z,t)+V(r)\psi(x,y,z,t)=i\hbar\frac{\partial}{\partial t}\psi(x,y,z,t)$$

Using the Laplacian operator, you can recast this into a more compact form. Here's what the Laplacian looks like:

$$\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)=\nabla^2$$

And here's the 3D Schrödinger equation using the Laplacian:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z,t)+V(x,y,z,t)\psi(x,y,z,t)=i\hbar\frac{\partial}{\partial t}\psi(x,y,z,t)$$

To solve this equation, when the potential doesn't vary with time, break out the time-dependent part of the wave function:

$$\psi(x,y,z,t)=\psi(x,y,z)e^{-iEt/\hbar}$$

Here, $\psi(x, y, z)$ is the solution of the time-independent Schrödinger equation, and E is the energy:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

So far, so good. But now you've run into a wall — the expression $\nabla^2\psi(x,y,z)$ is in general very hard to deal with, so the current equation is in general very hard to solve.

So what should you do? Well, you can focus on the case in which the equation is *separable* — that is, where you can separate out the x, y, and z dependence and find the solution in each dimension separately. In other words, in separable cases, the potential, V(x, y, z), is actually the sum of the x, y, and z potentials:

V(x, y, z) = V$_x$(x) + V$_y$(y) + V$_z$(z)

Now you can break the Hamiltonian in $\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\psi(x,y,z)$ $=E\psi(x,y,z)$ into three Hamilitonians, H$_x$, H$_y$, and H$_z$:

$$(H_x + H_y + H_z)\psi(x, y, z) = E\psi(x, y, z)$$

where

$$H_x = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(x)$$

$$H_y = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_y(y)$$

$$H_z = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V_z(z)$$

When you divide up the Hamiltonian as in $(H_x + H_y + H_z)\psi(x, y, z) = E\psi(x, y, z)$, you can also divide up the wave function that solves that equation. In particular, you can break the wave function into three parts, one for x, y, and z:

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

Where $X(x)$, $Y(y)$, and $Z(z)$ are functions of the coordinates x, y, and z and are not to be confused with the position operators. This separation of the wave function into three parts is going to make life considerably easier, because now you can break the Hamiltonian up into three separate operators added together:

$$\left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V_x(x)\right) + \left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2} + V_y(y)\right) + \left(\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2} + V_z(z)\right) = H$$

$$E = E_x + E_y + E_z$$

So you now have three independent Schrödinger equations for the three dimensions:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}X(x) + V(x)X(x) = E_x X(x)$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial y^2}Y(y) + V(y)Y(y) = E_y Y(y)$$

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial z^2}Z(z) + V(z)Z(z) = E_z Z(z)$$

This system of independent differential equations looks a lot easier to solve than $(H_x + H_y + H_z)\psi(x, y, z) = E\psi(x, y, z)$. In essence, you've broken the three-dimensional Schrödinger equation into three one-dimensional Schrödinger equations. That makes solving 3D problems tractable.

Solving Three-Dimensional Free Particle Problems

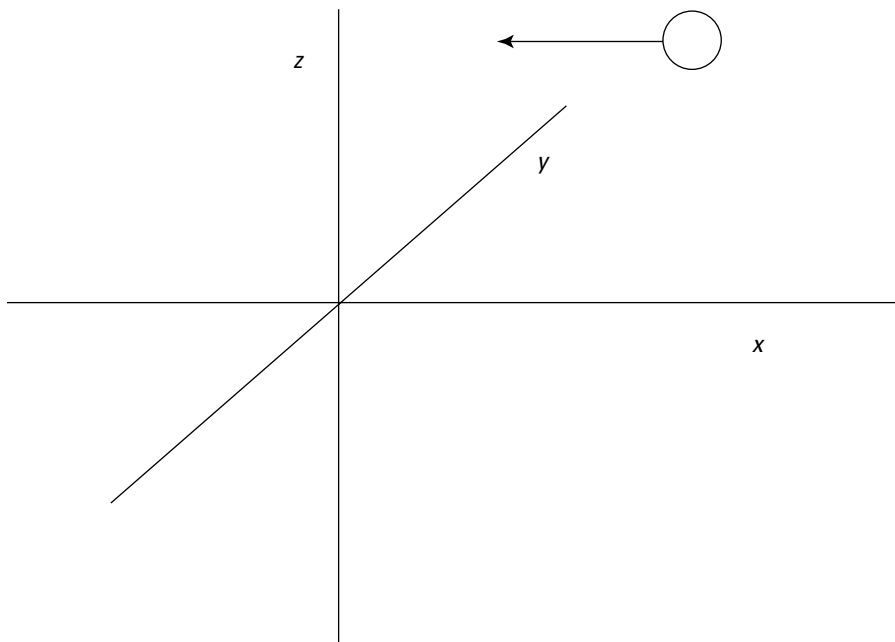Consider the free particle you see in three dimensions in Figure 7-1.

Figure 7-1:
A free
particle
in 3D.

Because the particle is traveling freely, $V(x) = V(y) = V(z) = 0$. So the three independent Schrödinger equations for the three dimensions covered in the preceding section become the following:

✔ $\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}X(x)=E_x X(x)$

✔ $\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial y^2}Y(y)=E_y Y(y)$

✔ $\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial z^2}Z(z)=E_z Z(z)$

If you rewrite these equations in terms of the wave number, k, where

$k^2 = \dfrac{2mE}{\hbar^2}$, then these equations become the following:

✔ $\dfrac{\partial^2}{\partial x^2}X(x)=-k_x{}^2 X(x)$

✔ $\dfrac{\partial^2}{\partial y^2}Y(y)=-k_y{}^2 Y(y)$

✔ $\dfrac{\partial^2}{\partial z^2}Z(z)=-k_z{}^2 Z(z)$

In this section, you take a look at the solutions to these equations, find the total energy, and add time dependence.

The x, y, and z equations

Take a look at the x equation for the free particle, $\dfrac{\partial^2}{\partial x^2}X(x)=-k_x{}^2 X(x)$. You can write its general solution as

$X(x) = A_x e^{ik_x x}$

$Y(y) = A_y e^{ik_y y}$

$Z(z) = A_z e^{ik_z z}$

where A_x, A_y, and A_z are constants.

Because $\psi(x, y, z) = X(x)Y(y)Z(z)$, you get this for $\psi(x, y, z)$:

$$\psi(x,y,z) = A_x A_y A_z e^{ik_x x} e^{ik_y y} e^{ik_z z}$$
$$= Ae^{i(k_x x + k_y y + k_z z)}$$

where $A = A_x A_y A_z$.

The part in the parentheses in the exponent is the dot product of the vectors $\boldsymbol{k}$ and $\boldsymbol{r}$, $\boldsymbol{k} \cdot \boldsymbol{r}$. That is, if the vector $\boldsymbol{a} = (a_x, a_y, a_z)$ in terms of components and the vector $\boldsymbol{b} = (b_x, b_y, b_z)$, then the dot product of $\boldsymbol{a}$ and $\boldsymbol{b}$ is $\boldsymbol{a} \cdot \boldsymbol{b} = (a_x b_x, a_y b_y, a_z b_z)$. So here's how you can rewrite the $\psi(x, y, z)$ equation:

$$\psi(x,y,z) = Ae^{i\boldsymbol{k} \cdot \boldsymbol{x}}$$

Finding the total energy equation

The total energy of the free particle is the sum of the energy in three dimensions:

$$E = E_x + E_y + E_z$$

With a free particle, the energy of the x component of the wave function is $\dfrac{\hbar^2 k_x^{\,2}}{2m} = E_x$. And this equation works the same way for the y and z components, so here's the total energy of the particle:

$$E = \frac{\hbar^2 k_x^{\,2}}{2m} + \frac{\hbar^2 k_y^{\,2}}{2m} + \frac{\hbar^2 k_z^{\,2}}{2m}$$
$$= \frac{\hbar^2}{2m}\left(k_x^{\,2} + k_y^{\,2} + k_z^{\,2}\right)$$

Note that $k_x^2 + k_y^2 + k_z^2$ is the square of the magnitude of **k** — that is, **k** $\cdot$ **k** $= k^2$. Therefore, you can write the equation for the total energy as

$$E = \frac{\hbar^2}{2m}\left(k_x^2 + k_y^2 + k_z^2\right) = \frac{\hbar^2}{2m}k^2$$

REMEMBER

Note that because E is a constant, no matter where the particle is pointed,

all the eigenfunctions of $\frac{\partial^2}{\partial x^2}X(x) = -k_x^2 X(x)$, $\frac{\partial^2}{\partial y^2}Y(y) = -k_y^2 Y(y)$, and

$\frac{\partial^2}{\partial z^2}Z(z) = -k_z^2 Z(z)$ are infinitely degenerate as you vary k_x, k_y, and k_z.

Adding time dependence and getting a physical solution

You can add time dependence to the solution for ψ(x, y, z), giving you ψ(x, y, z, t), if you remember that, for a free particle, $\psi(x,y,z,t) = \psi(x,y,z)e^{-iEt/\hbar}$. That equation gives

you this form for ψ(x, y, z, t):

$$\psi(x,y,z,t) = Ae^{i\left(\mathbf{k}\cdot\mathbf{r} - Et/\hbar\right)}$$

Because $\omega = \frac{E}{\hbar}$, the equation turns into

$$\psi(x,y,z,t) = Ae^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$$

In fact, now that the right side of the equation is in terms of the radius vector **r,** you can make the left side match:

$$\psi(\mathbf{r},t) = Ae^{i(\mathbf{k}\cdot\mathbf{r} - \omega t)}$$

That's the solution to the Schrödinger equation, but it's unphysical (as I discuss for the one-dimensional Schrödinger equation for a free particle in Chapter 3). Why? Trying to normalize this equation in three dimensions, for example, gives you the following, where A is a constant:

$$\int_{-\infty}^{+\infty}\psi(\boldsymbol{r},t)\psi^{*}(\boldsymbol{r},t)d^{3}r=|A|^{2}\int_{-\infty}^{+\infty}d^{3}r\to\infty$$

Thus, the integral diverges and you can't normalize $\psi(r,\,t)$ as I've written it. So what do you do here to get a physical particle?

The key to solving this problem is realizing that if you have a number of solutions to the Schrödinger equation, then any linear combination of those solutions is also a solution. In other words, you add various wave functions together so that you get a *wave packet,* which is a collection of wave functions of the form $e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$ such that

  ✔ The wave functions interfere constructively at one location.

  ✔ They interfere destructively (go to zero) at all other locations.

Look at the time-independent version:

$$\psi(\boldsymbol{r})=\sum_{n=1}^{\infty}\phi_{n}e^{i\boldsymbol{k}\cdot\boldsymbol{r}}$$

However, for a free particle, the energy states are not separated into distinct bands; the possible energies are continuous, so people write this summation as an integral:

$$\psi(\boldsymbol{r})=\frac{1}{(2\pi)^{3/2}}\int_{-\infty}^{+\infty}\phi(\boldsymbol{k})e^{i\boldsymbol{k}\cdot\boldsymbol{r}}d^{3}k$$

So what is $\phi(\boldsymbol{k})$? It's the three-dimensional analog of $\phi(k)$ that you find in Chapter 3; that is, it's the amplitude of each component wave function. You can find $\phi(\boldsymbol{k})$ from the Fourier transform of $\psi_{1}(x) = Ae^{ik_{1}x} + Be^{-ik_{1}x}$ (where $x < 0$) like this:

$$\phi(\boldsymbol{k})=\frac{1}{(2\pi)^{3/2}}\int_{-\infty}^{+\infty}\psi(\boldsymbol{r})e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}d^{3}k$$

In practice, you choose $\phi(\boldsymbol{k})$ yourself. Look at an example, using the following form for $\phi(\boldsymbol{k})$, which is for a Gaussian wave packet (***Note:*** The exponential part is what makes this a Gaussian wave form):

$$\phi(\boldsymbol{k})=\phi(k)=A\exp\left(\frac{-a^{2}k^{2}}{4}\right)$$

where a and A are constants. You can begin by normalizing $\phi(\boldsymbol{k})$ to determine what A is. Here's how that works:

$$1 = \int_{-\infty}^{+\infty} |\phi(k)|^2 \, d^3k = |A|^2 \int_{-\infty}^{+\infty} \exp\left(\frac{-a^2}{2} k^2\right) d^3k$$

Okay. Performing the integral gives you

$$1 = |A|^2 \left(\frac{2\pi}{a^2}\right)^{3/2}$$

$$A = \left(\frac{a^2}{2\pi}\right)^{3/4}$$

which means that the wave function is

$$\psi(\boldsymbol{r}, t) = \frac{1}{(2\pi)^{3/2}} \left(\frac{a^2}{2\pi}\right)^{3/4} \int_{-\infty}^{\infty} \exp\left(\frac{-a^2}{2} k^2\right) e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \, d^3k$$

You can evaluate this equation to give you the following, which is what the time-independent wave function for a Gaussian wave packet looks like in 3D:

$$\psi(\boldsymbol{r}, t) = \left(\frac{2}{\pi a^2}\right)^{3/4} \exp\left(\frac{-r^2}{a^2}\right)$$

Okay, that's how things look when V($\boldsymbol{r}$) = 0. But can't you solve some problems when V($\boldsymbol{r}$) is not equal to zero? Yep, you sure can. Check out the next section.

Getting Squared Away with 3D Rectangular Potentials

This section takes a look at a 3D potential that forms a box, as you see in Figure 7-2. You want to get the wave functions and the energy levels here.
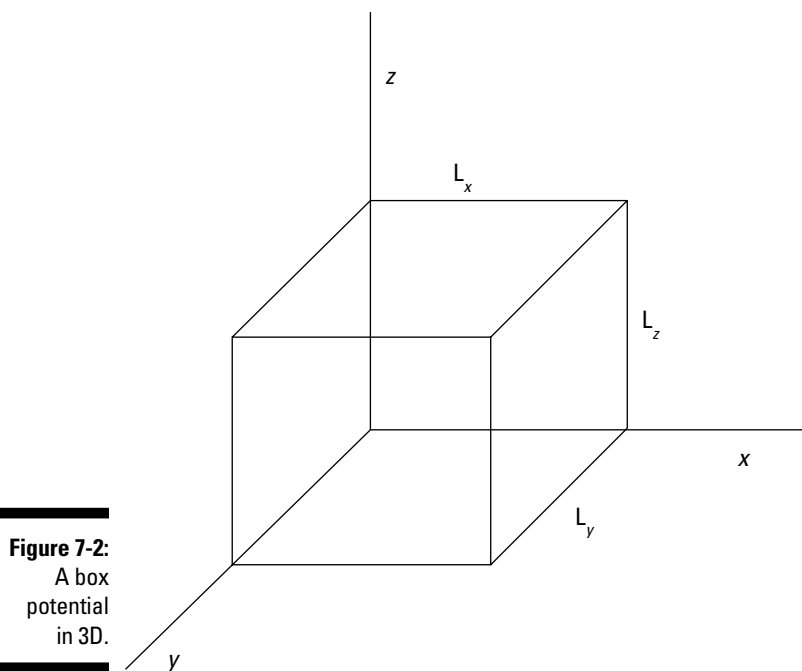
Figure 7-2:
A box
potential
in 3D.

Inside the box, say that V(x, y, z) = 0, and outside the box, say that V(x, y, z) = ∞. So you have the following:

$$V\left(x,y,z\right)= \begin{vmatrix} 0, \text{ where } 0 < x < \mathrm{L}_x,\ 0 < y < \mathrm{L}_y,\ 0 < z < \mathrm{L}_z \\ \infty \text{ otherwise} \end{vmatrix}$$

Dividing V(x, y, z) into $V_x(x)$, $V_y(y)$, and $V_z(z)$ gives you

✔ $V_x\left(x\right)= \begin{vmatrix} 0, \text{ where } 0 < x < \mathrm{L}_x \\ \infty \text{ otherwise} \end{vmatrix}$

✔ $V_y\left(y\right)= \begin{vmatrix} 0, \text{ where } 0 < y < \mathrm{L}_y \\ \infty \text{ otherwise} \end{vmatrix}$

✔ $V_z\left(z\right)= \begin{vmatrix} 0, \text{ where } 0 < z < \mathrm{L}_z \\ \infty \text{ otherwise} \end{vmatrix}$

Okay, because the potential goes to infinity at the walls of the box, the wave function, $\psi(x, y, z)$, must go to zero at the walls, so that's your constraint. In 3D, the Schrödinger equation looks like this in three dimensions:

$$\frac{-\hbar^2}{2m}\nabla^2\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

Writing this out gives you the following:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)+V(x,y,z)\psi(x,y,z)=E\psi(x,y,z)$$

Take this dimension by dimension. Because the potential is separable, you can write $\psi(x, y, z)$ as $\psi(x, y, z) = X(x)Y(y)Z(z)$. Inside the box, the potential equals zero, so the Schrödinger equation looks like this for *x, y,* and *z:*

✔ $\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}X(x)=E_xX(x)$

✔ $\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial y^2}Y(y)=E_yY(y)$

✔ $\dfrac{-\hbar^2}{2m}\dfrac{\partial^2}{\partial z^2}Z(z)=E_zZ(z)$

The next step is to rewrite these equations in terms of the wave number, *k.* Because $k^2=\dfrac{2mE}{\hbar^2}$, you can write the Schrödinger equations for *x, y,* and *z* as the following equations:

✔ $\dfrac{\partial^2}{\partial x^2}X(x)=-k_x^2X(x)$

✔ $\dfrac{\partial^2}{\partial y^2}Y(y)=-k_y^2Y(y)$

✔ $\dfrac{\partial^2}{\partial z^2}Z(z)=-k_z^2Z(z)$

Start by taking a look at the equation for x. Now you have something to work with — a second order differential equation, $\frac{\partial^2}{\partial x^2}X(x) = -k_x{}^2 X(x)$. Here are the two independent solutions to this equation, where A and B are yet to be determined:

- $X_1(x) = A \sin(kx)$
- $X_2(x) = B \cos(kx)$

So the general solution of $\frac{\partial^2}{\partial x^2}X(x) = -k_x{}^2 X(x)$ is the sum of the last two equations:

$$X(x) = A \sin(kx) + B \cos(kx)$$

Great. Now take a look at determining the energy levels.

Determining the energy levels

To be able to determine the energy levels of a particle in a box potential, you need an exact value for $X(x)$ — not just one of the terms of the constants A and B. You have to use the boundary conditions to find A and B. What are the boundary conditions? The wave function must disappear at the boundaries of the box, so

- $X(0) = 0$
- $X(L_x) = 0$

So the fact that $\psi(0) = 0$ tells you right away that B must be 0, because $\cos(0) = 1$. And the fact that $X(L_x) = 0$ tells you that $X(L_x) = A \sin(k_x L_x) = 0$. Because the sine is 0 when its argument is a multiple of π, this means that

$$k_x L_x = n_x \pi \qquad n_x = 1,2,3\ldots$$

$$k_x = \frac{n_x \pi}{L_x}$$

And because $k^2 = \frac{2mE}{\hbar^2}$, it means that

$$\frac{2mE_x}{\hbar^2} = \frac{n_x{}^2 \pi^2}{L_x{}^2} \qquad n_x = 1,2,3\ldots$$

$$E_x = \frac{n_x{}^2 \hbar^2 \pi^2}{2mL_x{}^2}$$

That's the energy in the x component of the wave function, corresponding to the quantum numbers 1, 2, 3, and so on. The total energy of a particle of mass m inside the box potential is $E = E_x + E_y + E_z$. Following $E_x = \dfrac{n_x^2 \hbar^2 \pi^2}{2mL_x^2}$, you have this for E_y and E_z:

$$E_y = \frac{n_y^2 \hbar^2 \pi^2}{2mL_y^2} \qquad n_y = 1,2,3\ldots$$

$$E_z = \frac{n_z^2 \hbar^2 \pi^2}{2mL_z^2} \qquad n_z = 1,2,3\ldots$$

So the total energy of the particle is $E = E_x + E_y + E_z$, which equals this:

$$E =$$
$$\frac{n_x^2 \hbar^2 \pi^2}{2mL_x^2} \qquad n_x = 1,2,3\ldots$$
$$+\frac{n_y^2 \hbar^2 \pi^2}{2mL_y^2} \qquad n_y = 1,2,3\ldots$$
$$+\frac{n_z^2 \hbar^2 \pi^2}{2mL_z^2} \qquad n_z = 1,2,3\ldots$$

And there you have the total energy of a particle in the box potential.

Normalizing the wave function

Now how about normalizing the wave function $\psi(x, y, z)$? In the x dimension, you have this for the wave equation:

$$X(x) = A \sin\left(\frac{n_x \pi x}{L_x}\right)$$

So the wave function is a sine wave, going to zero at $x = 0$ and $x = L_z$. You can also insist that the wave function be normalized, like this:

$$1 = \int_0^{L_x} \left|X(x)\right|^2 dx$$

By normalizing the wave function, you can solve for the unknown constant A. Substituting for X(x) in the equation gives you the following:

$$1 = |A|^2 \int_0^{L_x} \sin^2\left(\frac{n_x \pi x}{L_x}\right) dx$$

$$\int_0^{L_x} \sin^2\left(\frac{n_x \pi x}{L_x}\right) dx = \frac{L_x}{2}$$

Therefore, $1 = |A|^2 \int_0^{L_x} \sin^2\left(\frac{n_x \pi x}{L_x}\right) dx$ becomes $1 = |A|^2 \frac{L_x}{2}$, which means you can solve for A:

$$A = \left(\frac{2}{L_x}\right)^{1/2}$$

Great, now you have the constant A, so you can get X(x):

$$X(x) = \left(\frac{2}{L_x}\right)^{1/2} \sin\left(\frac{n_x \pi x}{L_x}\right) \quad n_x = 1,2,3\ldots$$

Now get $\psi(x, y, z)$. You can divide the wave function into three parts:

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

By analogy with X(x), you can find Y(y) and Z(z):

$$Y(y) = \left(\frac{2}{L_y}\right)^{1/2} \sin\left(\frac{n_y \pi y}{L_y}\right) \qquad n_y = 1,2,3\ldots$$

$$Z(z) = \left(\frac{2}{L_z}\right)^{1/2} \sin\left(\frac{n_z \pi z}{L_z}\right) \qquad n_z = 1,2,3\ldots$$

So $\psi(x, y, z)$ equals the following:

$$\psi(x,y,z) = \left(\frac{8}{L_x L_y L_z}\right)^{1/2} \sin\left(\frac{n_x \pi x}{L_x}\right)\sin\left(\frac{n_y \pi x}{L_y}\right)\sin\left(\frac{n_z \pi x}{L_z}\right)$$

$$n_x = 1,2,3\ldots$$
$$n_y = 1,2,3\ldots$$
$$n_z = 1,2,3\ldots$$

That's a pretty long wave function. In fact, when you're dealing with a box potential, the energy looks like this:

$$E =$$

$$\frac{n_x^2 \hbar^2 \pi^2}{2mL_x^2} \qquad n_x = 1,2,3\ldots$$

$$+\frac{n_y^2 \hbar^2 \pi^2}{2mL_y^2} \qquad n_y = 1,2,3\ldots$$

$$+\frac{n_z^2 \hbar^2 \pi^2}{2mL_z^2} \qquad n_z = 1,2,3\ldots$$

Using a cubic potential

When working with a box potential, you can make things simpler by assuming that the box is actually a cube. In other words, $L = L_x = L_y = L_z$. When the box is a cube, the equation for the energy becomes

$$E = \frac{\hbar^2 \pi^2}{2mL^2}\left(n_x^2 + n_y^2 + n_z^2\right)$$
$$n_x = 1,2,3\ldots$$
$$n_y = 1,2,3\ldots$$
$$n_z = 1,2,3\ldots$$

So, for example, the energy of the ground state, where $n_x = n_y = n_z = 1$, is given by the following, where E_{111} is the ground state:

$$E_{111} = \frac{3\hbar^2 \pi^2}{2mL^2}$$

Note that there's some degeneracy in the energies; for example, note that

- ✔ E_{211} ($n_x = 2$, $n_y = 1$, $n_z = 1$) is $E_{211} = \frac{6\hbar^2 \pi^2}{2mL^2}$

- ✔ E_{121} ($n_x = 1$, $n_y = 2$, $n_z = 1$) is $E_{121} = \frac{6\hbar^2 \pi^2}{2mL^2}$

- ✔ E_{112} ($n_x = 1$, $n_y = 1$, $n_z = 2$) is $E_{112} = \frac{6\hbar^2 \pi^2}{2mL^2}$

So $E_{211} = E_{121} = E_{112}$, which means that the first excited state is threefold degenerate, matching the threefold equivalence in dimensions.

REMEMBER

In general, when you have symmetry built into the physical layout (as you do when $L = L_x = L_y = L_z$), you have degeneracy.

The wave function for a cubic potential is also easier to manage than the wave function for a general box potential (where the sides aren't of the same length). Here's the wave function for a cubic potential:

$$\psi(x,y,z) = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{n_x \pi x}{L}\right) \sin\left(\frac{n_y \pi y}{L}\right) \sin\left(\frac{n_z \pi z}{L}\right)$$

$$n_x = 1,2,3\ldots$$
$$n_y = 1,2,3\ldots$$
$$n_z = 1,2,3\ldots$$

So, for example, here's the wave function for the ground state ($n_x = 1$, $n_y = 1$, $n_z = 1$), $\psi_{111}(x, y, z)$:

$$\psi_{211}(x,y,z) = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

And here's $\psi_{211}(x, y, z)$:

$$\psi_{211}(x,y,z) = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{2\pi x}{L}\right) \sin\left(\frac{\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$
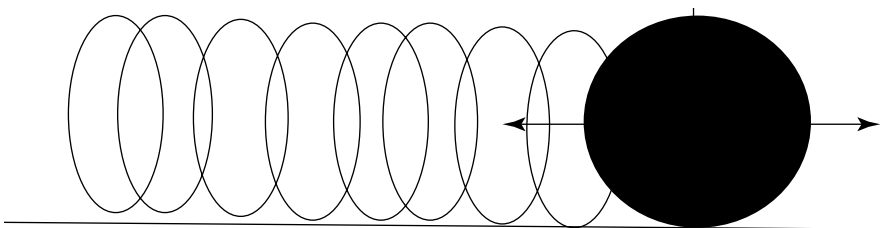
And $\psi_{121}(x, y, z)$:

$$\psi_{121}(x,y,z) = \left(\frac{8}{L^3}\right)^{1/2} \sin\left(\frac{\pi x}{L}\right) \sin\left(\frac{2\pi y}{L}\right) \sin\left(\frac{\pi z}{L}\right)$$

Springing into 3D Harmonic Oscillators

In one dimension, the general particle harmonic oscillator (which I first describe in Chapter 4) looks like Figure 7-3, where the particle is under the influence of a restoring force — here illustrated as a spring.

Figure 7-3:
A harmonic
oscillator.

The restoring force has the form $F_x = -k_x x$ in one dimension, where k_x is the constant of proportionality between the force on the particle and the location of the particle. The potential energy of the particle as a function of location x is $V(x) = \frac{1}{2} k_x x^2$. This is also sometimes written as

$$V(x) = \frac{1}{2} m \omega_x^2 x^2$$

where $\omega_x^2 = \frac{k_x}{m}$.

In this section, you take a look at the harmonic oscillator in three dimensions. In three dimensions, the potential looks like this:

$$V(x,y,z) = \frac{1}{2} m \omega_x^2 x^2 + \frac{1}{2} m \omega_y^2 y^2 + \frac{1}{2} m \omega_z^2 z^2$$

$$\omega_x^2 = \frac{k_x}{m}$$

$$\omega_y^2 = \frac{k_y}{m}$$

$$\omega_z^2 = \frac{k_z}{m}$$

Now that you have a form for the potential, you can start talking in terms of Schrödinger's equation:

$$\frac{-\hbar^2}{2m} \left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right) \psi(x,y,z) + V(x,y,z) \psi(x,y,z) = E \psi(x,y,z)$$

Substituting in for the three-dimension potential, $V(x, y, z)$, gives you this equation:

$$\frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)\psi(x,y,z)$$
$$+\left(\frac{1}{2}m\omega_x^2 x^2+\frac{1}{2}m\omega_y^2 y^2+\frac{1}{2}m\omega_z^2 z^2\right)\psi(x,y,z)=E\psi(x,y,z)$$

Take this dimension by dimension. Because you can separate the potential into three dimensions, you can write $\psi(x, y, z)$ as $\psi(x, y, z) = X(x)Y(y)Z(z)$. Therefore, the Schrödinger equation looks like this for x:

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}X(x)+\frac{1}{2}m\omega_x^2 x^2 X(x)=E_x X(x)$$

You solve that equation in Chapter 4, where you get this next solution:

$$X(x)=\frac{1}{\pi^{1/4}\left(2^{n_x}n_x!x_0\right)^{1/2}}H_{n_x}\left(\frac{x}{x_0}\right)\exp\left(\frac{-x^2}{2x_{x0}^2}\right)$$

where $x_0=\left(\frac{\hbar}{m\omega_x}\right)^{\frac{1}{2}}$ and $n_x = 0, 1, 2$, and so on. The H_{n_x} term indicates a

hermite polynomial, which looks like this:

- ✔ $H_0(x) = 1$
- ✔ $H_1(x) = 2x$
- ✔ $H_2(x) = 4x^2 - 2$
- ✔ $H_3(x) = 8x^3 - 12x$
- ✔ $H_4(x) = 16x^4 - 48x^2 + 12$
- ✔ $H_5(x) = 32x^5 - 160x^3 + 120x$

Therefore, you can write the wave function like this:

$$\psi(x,y,z)=\frac{1}{\pi^{3/4}}\frac{1}{\left(2^{n_x+n_y+n_z}n_x!n_y!n_z!x_0 y_0 z_0\right)^{1/2}}H_{n_x}\left(\frac{x}{x_0}\right)H_{n_y}\left(\frac{y}{y_0}\right)H_{n_z}\left(\frac{z}{z_0}\right)\exp\left(-\frac{x^2}{2x_0^2}-\frac{y^2}{2y_0^2}-\frac{z^2}{2z_0^2}\right)$$

That's a relatively easy form for a wave function, and it's all made possible by the fact that you can separate the potential into three dimensions.

What about the energy of the harmonic oscillator? The energy of a one-dimensional harmonic oscillator is $E = \left(n + \frac{1}{2} \right) \hbar \omega$. And by analogy, the energy of a three-dimensional harmonic oscillator is given by

$$E = \left(n_x + \frac{1}{2} \right) \hbar \omega_x + \left(n_y + \frac{1}{2} \right) \hbar \omega_y + \left(n_z + \frac{1}{2} \right) \hbar \omega_z$$

Note that if you have an isotropic harmonic oscillator, where $\omega_x = \omega_y = \omega_z = \omega$, the energy looks like this:

$$E = \left(n_x + n_y + n_z + \frac{3}{2} \right) \hbar \omega$$

As for the cubic potential, the energy of a 3D isotropic harmonic oscillator is degenerate. For example, $E_{112} = E_{121} = E_{211}$. In fact, it's possible to have more than threefold degeneracy for a 3D isotropic harmonic oscillator — for example, $E_{200} = E_{020} = E_{002} = E_{110} = E_{101} = E_{011}$.

In general, the degeneracy of a 3D isotropic harmonic oscillator is

$$\text{Degeneracy} = \frac{1}{2}(n+1)(n+2)$$

where $n = n_x + n_y + n_z$.

Chapter 8

Solving Problems in Three Dimensions: Spherical Coordinates

In This Chapter

▶ Problems in spherical coordinates

▶ Free particles in spherical coordinates

▶ Square well potentials

▶ Isotropic harmonic oscillators

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*1*n your other life as a sea captain-slash-pilot, you're probably pretty familiar with latitude and longitude — coordinates that basically name a couple of angles as measured from the center of the Earth. Put together the angle east or west, the angle north or south, and the all-important distance from the center of the Earth, and you have a vector that gives a good description of location in three dimensions. That vector is part of a *spherical coordinate system*.

Navigators talk more about the pair of angles than the distance ("Earth's surface" is generally specific enough for them), but quantum physicists find both angles and radius length important. Some 3D quantum physics problems even allow you to break down a wave function into two parts: an angular part and a radial part.

In this chapter, I discuss three-dimensional problems that are best handled using spherical coordinates. (For 3D problems that work better in rectangular coordinate systems, see Chapter 7.)

A New Angle: Choosing Spherical Coordinates Instead of Rectangular

Say you have a 3D box potential, and suppose that the potential well that the particle is trapped in looks like this, which is suited to working with rectangular coordinates:

$$V(x,y,z) = \begin{vmatrix} 0, \text{ where } 0 < x < L_x, \ 0 < y < L_y, \ 0 < z < L_z \\ \infty \text{ otherwise} \end{vmatrix}$$

Because you can easily break this potential down in the x, y, and z directions, you can break the wave function down that way, too, as you see here:

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

Solving for the wave function gives you the following normalized result in rectangular coordinates:

$$\psi(x,y,z) = \left(\frac{8}{L_x L_y L_z} \right)^{\frac{1}{2}} \sin \frac{(n_x \pi x)}{L_x} \sin \frac{(n_y \pi y)}{L_y} \sin \frac{(n_z \pi z)}{L_z}$$

$$n_x = 1,2,3\ldots$$
$$n_y = 1,2,3\ldots$$
$$n_z = 1,2,3\ldots$$

The energy levels also break down into separate contributions from all three rectangular axes:

$$E = E_x + E_y + E_z$$

And solving for E gives you this equation (from Chapter 7):

$$E =$$
$$\frac{n_x^2 \hbar^2 \pi^2}{2mL_x^2} \qquad n_x = 1,2,3\ldots$$
$$+\frac{n_y^2 \hbar^2 \pi^2}{2mL_y^2} \qquad n_y = 1,2,3\ldots$$
$$+\frac{n_z^2 \hbar^2 \pi^2}{2mL_z^2} \qquad n_z = 1,2,3\ldots$$

But what if the potential well a particle is trapped in has spherical symmetry, not rectangular? For example, what if the potential well were to look like this, where r is the radius of the particle's location with respect to the origin and where a is a constant?

$$V(r) = \begin{vmatrix} 0, \text{ where } 0 < r < a \\ \infty \text{ otherwise} \end{vmatrix}$$

Clearly, trying to stuff this kind of problem into a rectangular-coordinates kind of solution is only asking for trouble, because although you can do it, it involves lots of sines and cosines and results in a pretty complex solution. A much better tactic is to solve this kind of a problem in the natural coordinate system in which the potential is expressed: spherical coordinates.

REMEMBER

Figure 8-1 shows the spherical coordinate system along with the corresponding rectangular coordinates, $x, y,$ and z. In the spherical coordinate system, you locate points with a radius vector named $\boldsymbol{r}$, which has three components:

- ✔ An r component (the length of the radius vector)
- ✔ θ (the angle from z axis to the the $\boldsymbol{r}$ vector)
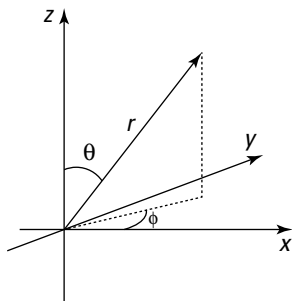- ✔ ϕ (the angle from the x axis to the the $\boldsymbol{r}$ vector)

Figure 8-1:
The spherical coordinate system.

Taking a Good Look at Central Potentials in 3D

This chapter focuses on problems that involve *central potentials* — that is, spherically symmetrical potentials, of the kind where V(**r**) = V(r). In other words, the potential is independent of the vector nature of the radius vector; the potential depends on only the magnitude of vector **r** (which is r), not on the angle of **r.**

When you work on problems that have a central potential, you're able to separate the wave function into a radial part (which depends on the form of the potential) and an angular part, which is a spherical harmonic. Read on.

Breaking down the Schrödinger equation

The Schrödinger equation looks like this in three dimensions, where Δ is the Laplacian operator (see Chapter 2 for more on operators):

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

And the Laplacian operator looks like this in rectangular coordinates:

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

In spherical coordinates, it's a little messy, but you can simplify later. Check out the spherical Laplacian operator:

$$\nabla^2=\frac{1}{r}\frac{\partial^2}{\partial r^2}r-\frac{1}{\hbar^2r^2}\mathrm{L}^2$$

Here, **L**^{2} is the square of the orbital angular momentum:

$$\mathbf{L}^2=-\hbar^2\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)$$

So in spherical coordinates, the Schrödinger equation for a central potential looks like this when you substitute in the terms:

$$\frac{-\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi(\boldsymbol{r})+\frac{1}{2mr^2}\mathbf{L}^2\psi(\boldsymbol{r})+\mathrm{V}(\boldsymbol{r})\psi(\boldsymbol{r})=\mathrm{E}\psi(\boldsymbol{r})$$

REMEMBER

Take a look at the preceding equation. The first term actually corresponds to the *radial kinetic energy* — that is, the kinetic energy of the particle moving in the radial direction. The second term corresponds to the *rotational kinetic energy*. And the third term corresponds to the *potential energy*.

So what can you say about the solutions to this version of the Schrödinger equation? You can note that the first term depends only on *r,* as does the third, and that the second term depends only on angles. So you can break the wave function, $\psi(\boldsymbol{r}) = \psi(r, \theta, \phi)$, into two parts:

    ✔ A radial part

    ✔ A part that depends on the angles

This is a special property of problems with central potentials.

The angular part of $\psi(r, \theta, \phi)$

When you have a central potential, what can you say about the angular part of $\psi(r, \theta, \phi)$? The angular part must be an eigenfunction of $\mathbf{L}^2$, and as I show in Chapter 5, the eigenfunctions of $\mathbf{L}^2$ are the spherical harmonics, $Y_{lm}(\theta, \phi)$ (where *l* is the total angular momentum quantum number and *m* is the *z* component of the angular momentum's quantum number). The spherical harmonics equal

$$Y_{lm}(\theta,\phi)=(-1)^{|m|}\left[\frac{(2l+1)(l-|m|)!}{4\pi(l+|m|)!}\right]^{\frac{1}{2}}P_{lm}(\cos\theta)e^{im\phi}$$

Here are the first several normalized spherical harmonics:

    ✔ $Y_{00}(\theta,\phi)=\dfrac{1}{(4\pi)^{\frac{1}{2}}}$

    ✔ $Y_{10}(\theta, \phi)=\left(\dfrac{3}{4\pi}\right)^{\frac{1}{2}}\cos\theta$

    ✔ $Y_{1\pm1}(\theta,\phi)=\pm\left(\dfrac{3}{8\pi}\right)^{\frac{1}{2}}e^{\pm i\phi}\sin\theta$

    ✔ $Y_{20}(\theta, \phi)=\left(\dfrac{5}{16\pi}\right)^{\frac{1}{2}}(3\cos^2\theta-1)$

    ✔ $Y_{2\pm1}(\theta,\phi)=\mp\left(\dfrac{15}{8\pi}\right)^{\frac{1}{2}}e^{\pm i\phi}\sin\theta\cos\theta$

    ✔ $Y_{2\pm2}(\theta, \phi)=\left(\dfrac{15}{32\pi}\right)^{\frac{1}{2}}e^{\pm 2i\phi}\sin^2\theta$

That's what the angular part of the wave function is going to be: a spherical harmonic.

The radial part of ψ (r, θ, φ)

You can give the radial part of the wave function the name $R_{nl}(r)$, where n is a quantum number corresponding to the quantum state of the radial part of the wave function and l is the total angular momentum quantum number. The radial part is symmetric with respect to angles, so it can't depend on m, the quantum number of the z component of the angular momentum. In other words, the wave function for particles in central potentials looks like the following equation in spherical coordinates:

$$\psi(r,\ \theta,\ \phi) = R_{nl}(r)Y_{lm}(\theta,\ \phi)$$

The next step is to solve for $R_{nl}(r)$ in general. Substituting $\psi(r,\ \theta,\ \phi)$ from the preceding equation into the Schrödinger equation,

$$\frac{-\hbar^2}{2m}\frac{1}{r}\frac{\partial^2}{\partial r^2}r\psi(\boldsymbol{r})+\frac{1}{2mr^2}\mathbf{L}^2\psi(\boldsymbol{r})+\mathrm{V}(\boldsymbol{r})\psi(\boldsymbol{r})=\mathrm{E}\psi(\boldsymbol{r}),$$ gives you

$$-\hbar^2\frac{r}{\mathrm{R}_{nl}(r)}\frac{d^2}{dr^2}\left[r\,\mathrm{R}_{nl}(r)\right]+2mr^2\left[\mathrm{V}(r)-\mathrm{E}\right]+\frac{\mathrm{L}^2\mathrm{Y}_{lm}(\theta,\phi)}{\mathrm{Y}_{lm}(\theta,\phi)}=0$$

Okay, what can you make of this? First, note (from Chapter 5) that the spherical harmonics are eigenfunctions of L^2 (that's the whole reason for using them), with eigenvalue $l(l + 1)\hbar^2$:

$$\mathrm{L}^2\mathrm{Y}_{lm}(\theta,\phi)=l(l+1)\hbar^2\mathrm{Y}_{lm}(\theta,\phi)$$

So the last term in this equation is simply $l(l + 1)\hbar^2$. That means that

$$-\hbar^2\frac{r}{\mathrm{R}_{nl}(r)}\frac{d^2}{dr^2}\left[r\,\mathrm{R}_{nl}(r)\right]+2mr^2\left[\mathrm{V}(r)-\mathrm{E}\right]+\frac{\mathrm{L}^2\mathrm{Y}_{lm}(\theta,\phi)}{\mathrm{Y}_{lm}(\theta,\phi)}=0$$ takes the form

$$-\hbar^2\frac{r}{\mathrm{R}_{nl}(r)}\frac{d^2}{dr^2}\left[r\,\mathrm{R}_{nl}(r)\right]+2mr^2\left[\mathrm{V}(r)-\mathrm{E}\right]+l(l+1)\hbar^2=0,$$ which equals

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

REMEMBER

The preceding equation is the one you use to determine the radial part of the wave function, $R_{nl}(r)$. It's called the *radial equation* for a central potential.

When you solve the radial equation for $R_{nl}(r)$, you can then find $\psi(r, \theta, \phi)$ because you already know $Y_{lm}(\theta,\phi)$:

$$\psi(r,\ \theta,\ \phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

Thus, this chapter simply breaks down to finding the solution to the radial equation.

Note: Incidentally, the radial equation is really a differential equation in one dimension: the *r* dimension. By selecting only problems that contain central potentials, you reduce the general problem of finding the wave function of particles trapped in a three-dimensional spherical potential to a one-dimensional differential equation.

Handling Free Particles in 3D with Spherical Coordinates

In this section and the next, you take a look at some example central potentials to see how to solve the radial equation (see the preceding section for more on the radial part). Here, you work with a free particle, in which no potential at all constrains the particle.

The wave function in spherical coordinates takes this form:

$$\psi(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

And you know all about $Y_{lm}(\theta, \phi)$, because it gives you the spherical harmonics. The problem is now to solve for the radial part, $R_{nl}(r)$. Here's the radial equation:

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

For a free particle, $V(r) = 0$, so the radial equation becomes

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

The way you usually handle this equation is to substitute ρ for kr, where $k = (2mE)^{1/2}/\hbar$, and because we have a version of the same equation for each n index it is convenient to simply remove it, so that $R_{nl}(r)$ becomes $R_l(kr) = R_l(\rho)$. This substitution means that

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}\left[rR_{nl}(r)\right] + \frac{l(l+1)\hbar^2}{2mr^2}\left[rR_{nl}(r)\right] = E\left[rR_{nl}(r)\right] \text{ becomes the following:}$$

$$\frac{d^2R_l(\rho)}{d\rho^2} + \frac{2}{\rho}\frac{dR_l(\rho)}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]R_l(\rho) = 0$$

In this section, you see how the spherical Bessel and Neumann functions come to the rescue when you're dealing with free particles.

The spherical Bessel and Neumann functions

The radial part of the equation, $\dfrac{d^2R_l(\rho)}{d\rho^2} + \dfrac{2}{\rho}\dfrac{dR_l(\rho)}{d\rho} + \left[1 - \dfrac{l(l+1)}{\rho^2}\right]R_l(\rho) = 0$,

looks tough, but the solutions turn out to be well-known — this equation is called the *spherical Bessel equation,* and the solution is a combination of the spherical Bessel functions [$j_l(\rho)$] and the spherical Neumann functions [$n_l(\rho)$]:

REMEMBER

$$R_l(\rho) = A_l j_l(\rho) + B_l n_l(\rho)$$

where A_l and B_l are constants. So what are the spherical Bessel functions and the spherical Neumann functions? The spherical Bessel functions are given by

$$j_l(\rho) = (-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\sin\rho}{\rho}$$

Here's what the first few iterations of $j_l(\rho)$ look like:

- ✔ $j_0(\rho) = \dfrac{\sin\rho}{\rho}$

- ✔ $j_1(\rho) = \dfrac{\sin\rho}{\rho^2} - \dfrac{\cos\rho}{\rho}$

- ✔ $j_2(\rho) = \dfrac{3\sin\rho}{\rho^3} - \dfrac{3\cos\rho}{\rho^2} - \dfrac{\sin\rho}{\rho}$

How about the spherical Neumann functions? The spherical Neumann functions are given by

$$n_l(\rho) = -(-\rho)^l\left(\frac{1}{\rho}\frac{d}{d\rho}\right)^l\frac{\cos\rho}{\rho}$$

Here are the first few iterations of $n_l(\rho)$:

✔ $n_0(\rho) = -\dfrac{\cos\rho}{\rho}$

✔ $n_1(\rho) = -\dfrac{\cos\rho}{\rho^2} - \dfrac{\sin\rho}{\rho}$

✔ $n_2(\rho) = -\dfrac{3\cos\rho}{\rho^3} - \dfrac{3\sin\rho}{\rho^2} + \dfrac{\cos\rho}{\rho}$

The limits for small and large ρ

According to the spherical Bessel equation, the radial part of the wave function for a free particle looks like this:

$$R_l(\rho) = A_l j_l(\rho) + B_l n_l(\rho)$$

Take a look at the spherical Bessel functions and Neumann functions for small and large ρ:

✔ **Small ρ:** The Bessel functions reduce to $j_l(\rho) \approx \dfrac{2^l l! \rho^l}{(2^l + 1)!}$.

The Neumann functions reduce to $n_l(\rho) \approx \dfrac{-(2l-1)! \rho^{-l-1}}{2^l l!}$.

✔ **Large ρ:** The Bessel functions reduce to $j_l(\rho) \approx \dfrac{1}{\rho} \sin\left(\rho - \dfrac{l\pi}{2}\right)$.

The Neumann functions reduce to $n_l(\rho) \approx -\dfrac{1}{\rho} \cos\left(\rho - \dfrac{l\pi}{2}\right)$.

WARNING!

Note that the Neumann functions diverge for small ρ. Therefore, any wave function that includes the Neumann functions also diverges, which is unphysical. So the Neumann functions aren't acceptable functions in the wave function.

That means the wave function $\psi(r, \theta, \phi)$, which equals $R_{nl}(r) Y_{lm}(\theta, \phi)$, equals the following:

$$\psi(r, \theta, \phi) = A_l j_l(kr) Y_{lm}(\theta, \phi)$$

where $k = (2mE_n)^{1/2}/\hbar$. Note that because k can take any value, the energy levels are continuous.

Handling the Spherical Square Well Potential

Take a look at a spherical square well potential of the kind you can see in Figure 8-2 (I introduce square wells in Chapter 3). This potential traps particles inside it when E < 0 and scatters particles when E > 0. Mathematically, you can express the square well potential like this:

$$V(r) = \begin{vmatrix} -V_0, \text{ where } 0 < r < a \\ 0, \text{ where } r > a \end{vmatrix}$$

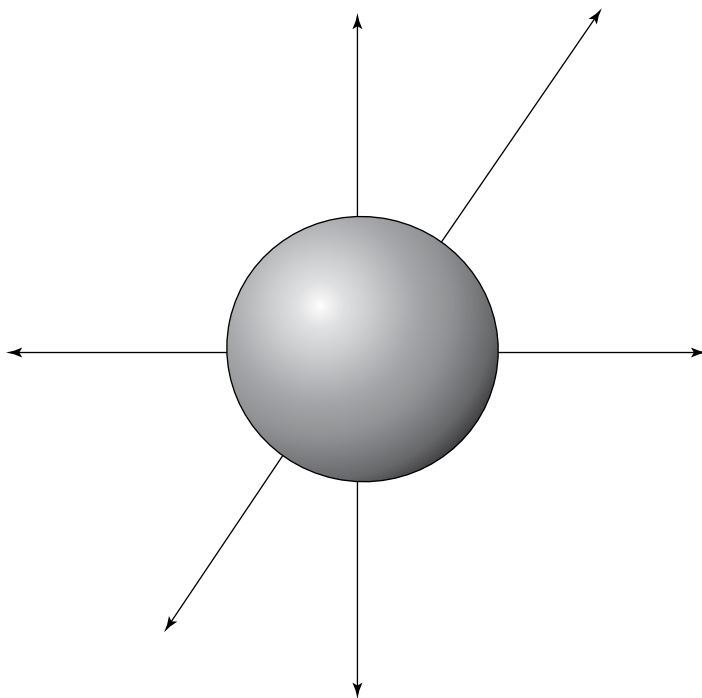**Figure 8-2:**
The spherical square well potential.

Note that this potential is spherically symmetric and varies only in r, not in θ or ϕ. You're dealing with a central potential, so you can break the wave function into an angular part and a radial part (see the earlier section "Taking a Good Look at Central Potentials in 3D").

This section has you take a look at the radial equation, handling the two cases of $0 < r < a$ and $r > a$ separately.

Inside the square well: 0 < r < a

For a spherical square well potential, here's what the radial equation looks like for the region $0 < r < a$:

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

In this region, $V(r) = -V_0$, so you have

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}\left[r\,R_{nl}(r)\right]+\left[-V_0+\frac{l(l+1)\hbar^2}{2mr^2}\right]\left[r\,R_{nl}(r)\right]=E\left[r\,R_{nl}(r)\right]$$

Taking the V_0 term over to the right gives you the following:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}\left[r\,R_{nl}(r)\right]+\frac{l(l+1)\hbar^2}{2mr^2}\left[r\,R_{nl}(r)\right]=(E+V_0)r\,R_{nl}(r)$$

And here's what dividing by r gives you:

$$\frac{-\hbar^2}{2m}\frac{1}{r}\frac{d^2}{dr^2}\left[r\,R_{nl}(r)\right]+\frac{l(l+1)\hbar^2}{2mr^2}R_{nl}(r)=(E+V_0)R_{nl}(r)$$

Then, multiplying by $-2m/\hbar^2$, you get

$$\frac{1}{r}\frac{d^2}{dr^2}\left[r\,R_{nl}(r)\right]-\frac{l(l+1)}{r^2}R_{nl}(r)=-\frac{2m}{\hbar^2}(E+V_0)R_{nl}(r)$$

Now make the change of variable $\rho = kr$, where $k = (2m(E+V_0))^{1/2}/\hbar$, so that $R_{nl}(r)$ becomes $R_l(kr) = R_l(\rho)$. Using this substitution means that
$V(r)=\begin{vmatrix}-V_0, \text{ where } 0 < r < a \\ 0, \text{ where } r > a\end{vmatrix}$ takes the following form:

$$\frac{d^2R_l(\rho)}{d\rho^2}+\frac{2}{\rho}\frac{dR_l(\rho)}{d\rho}+\left[1-\frac{l(l+1)}{\rho^2}\right]R_l(\rho)=0$$

This is the spherical Bessel equation (just as you see for the free particle in "Handling Free Particles in 3D with Spherical Coordinates"). This time, $k = [2m(E+V_0)]^{1/2}/\hbar$, not $(2mE)^{1/2}/\hbar$. That makes sense, because now the particle is trapped in the square well, so its total energy is $E + V_0$, not just E.

The solution to the preceding equation is a combination of the spherical Bessel functions [$j_l(\rho)$] and the spherical Neumann functions [$n_l(\rho)$]:

$R_l(\rho) = A_l j_l(\rho) + B_l n_l(\rho)$

You can apply the same constraint here that you apply for a free particle: The wave function must be finite everywhere. For small ρ, the Bessel functions look like this:

$$j_l(\rho) \approx \frac{2^l l! \rho^l}{(2^l + 1)!}$$

And for small ρ, the Neumann functions reduce to

$$n_l(\rho) \approx \frac{-(2l-1)! \rho^{-l-1}}{2^l l!}$$

So the Neumann functions diverge for small ρ, which makes them unacceptable for wave functions here. That means that the radial part of the wave function is just made up of spherical Bessel functions, where A_l is a constant:

$R_l(\rho) = A_l j_l(\rho)$

The whole wave function inside the square well, $\psi_{inside}(r,\ \theta,\ \phi)$, is a product of radial and angular parts, and it looks like this:

$$\psi_{inside}(r, \theta, \phi) = A_l j_l(\rho_{inside}) Y_{lm}(\theta, \phi)$$

where $\rho_{inside} = r(2m(E + V_0))^{1/2}/\hbar$ and $Y_{lm}(\theta,\ \phi)$ are the spherical harmonics.

Outside the square well: r > a

Outside the square well, in the region $r > a$, the particle is just like a free particle, so here's what the radial equation looks like:

$$\frac{-\hbar^2}{2m} \frac{d^2}{dr^2}[r\, R_{nl}(r)] + \left[\frac{l(l+1)\hbar^2}{2mr^2}\right][r\, R_{nl}(r)] = E\left[r\, R_{nl}(r)\right]$$

You solve this equation earlier in "Handling Free Particles in 3D with Spherical Coordinates": Because $\rho = kr$, where $k = (2mE)^{1/2}/\hbar$, you substitute ρ for kr so that $R_{nl}(r)$ becomes $R_l(kr) = R_l(\rho)$. Using this substitution means that the radial equation takes the following form:

$$\frac{d^2 R_l(\rho)}{d\rho^2} + \frac{2}{\rho}\frac{dR_l(\rho)}{d\rho} + \left[1 - \frac{l(l+1)}{\rho^2}\right]R_l(\rho) = 0$$

The solution is a combination of spherical Bessel functions and spherical Neumann functions, where B_l and C_l are constants:

$$R_l(r) = B_l j_l(\rho_{outside}) + C_l n_l(\rho_{outside})$$

If the energy E < 0, we must have C_l = i B_l'' so that the wave function decays exponentially at large distances r. So the radial solution outside the square well looks like this, where $\rho_{outside} = r(2mE)^{1/2}/\hbar$:

$$\psi_{outside}(r,\theta,\phi) = \left[B_l j_l(\rho_{outside}) + C_l n_l(\rho_{outside})\right]Y_{lm}(\theta,\phi)$$

From the preceding section, you know that the wave function inside the square well is

$$\psi_{inside}(r,\theta,\phi) = A_l j_l(\rho_{inside})Y_{lm}(\theta,\phi)$$

So how do you find the constants A_l, B_l, and C_l? You find those constants through continuity constraints: At the inside/outside boundary, where $r = a$, the wave function and its first derivative must be continuous. So to determine the constants you have to solve these two equations:

$$\left|\begin{array}{l} \blacktriangleright \ \psi_{inside}(a,\theta,\phi) = \psi_{outside}(a,\theta,\phi) \\ \blacktriangleright \ \dfrac{d}{dr}\psi_{inside}(r,\theta,\phi)\Big|_{r=a} = \dfrac{d}{dr}\psi_{outside}(r,\theta,\phi)\Big|_{r=a} \end{array}\right.$$

Getting the Goods on Isotropic Harmonic Oscillators

This section takes a look at spherically symmetric harmonic oscillators in three dimensions. In one dimension, you write the harmonic oscillator potential like this:

$$V(x) = \frac{1}{2}m\omega^2 x^2$$

where $\omega^2 = \dfrac{k}{m}$ (here, k is the spring constant; that is, the restoring force of the harmonic oscillator is F = $-kx$). You can turn these two equations into three-dimensional versions of the harmonic potential by replacing x with r:

$$V(r) = \frac{1}{2}m\omega^2 r^2$$

where $\omega^2 = \frac{k}{m}$. Because this potential is spherically symmetric, the wave function is going to be of the following form:

$$\psi(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)$$

where you have yet to solve for the radial function $R_{nl}(r)$ and where $Y_{lm}(\theta, \phi)$ describes the spherical harmonics.

As you know, the radial Schrödinger equation looks like this:

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

Substituting for V(r) from $V(r) = \frac{1}{2}m\omega^2 r^2$ gives you the following:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}[r\,R_{nl}(r)] + \left[\frac{1}{2}m\omega^2 r^2 + \frac{l(l+1)\hbar^2}{2mr^2}\right][r\,R_{nl}(r)] = E[r\,R_{nl}(r)]$$

Well, the solution to this equation is pretty difficult to obtain, and you're not going to gain anything by going through the math (pages and pages of it), so here's the solution:

$$R_{nl}(r) = C_{nl}r^l\exp\left(-m\omega\frac{r^2}{2\hbar}\right)L_n^{l+\frac{1}{2}}\left(m\omega\frac{r^2}{\hbar}\right)$$

where $\exp(x) = e^x$ and

$$C_{nl} = \frac{\left[\frac{2^{n+l+2}\left(\frac{m\omega}{\hbar}\right)^{l+\frac{3}{2}}}{\pi^{\frac{1}{2}}}\right]^{\frac{1}{2}}\left[\frac{n-l}{2}\right]!\left[\frac{n+l}{2}\right]!}{\left[(n+l+1)!\right]^{\frac{1}{2}}}$$

And the $L_a^b(r)$ functions are the generalized Laguerre polynomials:

$$L_a^b(r) = \frac{r^{-b}e^r}{a!}\frac{d^a}{dr^a}\left(e^{-r}r^{a+b}\right)$$

Wow. Aren't you glad you didn't slog through the math? Here are the first few generalized Laguerre polynomials:

$$✔ L_0^b(r) = 1$$

$$✔ L_1^b(r) = -r + b + 1$$

$$✔ L_2^b(r) = \frac{r^2}{2} - (b+2)r + \frac{(b+2)(b+1)}{2}$$

$$✔ L_3^b(r) = -\frac{r^3}{6} + \frac{(b+3)r^2}{2} - \frac{(b+2)(b+3)r}{2} + \frac{(b+1)(b+2)(b+3)}{6}$$

All right, you have the form for $R_{nl}(r)$. To find the complete wave function, $\psi_{nlm}(r, \theta, \phi)$, you multiply by the spherical harmonics, $Y_{lm}(\theta, \phi)$:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) Y_{lm}(\theta, \phi)$$

Now take a look at the first few wave functions for the isotropic harmonic oscillator in spherical coordinates:

$$✔ \psi_{00m}(r, \theta, \phi) = \frac{2}{\pi^{\frac{1}{4}}} \left(\frac{m\omega}{\hbar}\right)^{\frac{3}{4}} \exp\left(-m\omega \frac{r^2}{2\hbar}\right) Y_{0m}(\theta, \phi)$$

$$✔ \psi_{11m}(r, \theta, \phi) = \frac{\left(\frac{5}{3}\right)^{\frac{1}{2}}}{\pi^{\frac{1}{4}}} \left(\frac{m\omega}{\hbar}\right)^{\frac{5}{4}} r \left(5 - \frac{2m\omega r^2}{\hbar}\right) \exp\left(-m\omega \frac{r^2}{2\hbar}\right) Y_{1m}(\theta, \phi)$$

$$✔ \psi_{20m}(r, \theta, \phi) = \frac{1}{24^{\frac{1}{2}} \pi^{\frac{1}{4}}} \left(\frac{m\omega}{\hbar}\right)^{\frac{3}{4}} \left(15 - 20\frac{m\omega r^2}{\hbar} - 4\frac{m^2\omega^2 r^4}{\hbar^2}\right) \exp\left(-m\omega \frac{r^2}{2\hbar}\right) Y_{0m}(\theta, \phi)$$

$$✔ \psi_{21m}(r, \theta, \phi) = \pi^{\frac{3}{4}} \frac{3^{\frac{1}{2}}}{32} \left(\frac{m\omega}{\hbar}\right)^{\frac{5}{4}} r \left(35 - 28\frac{m\omega r^2}{\hbar} - 4\frac{m^2\omega^2 r^4}{\hbar^2}\right) \exp\left(-m\omega \frac{r^2}{2\hbar}\right) Y_{1m}(\theta, \phi)$$

As you can see, when you have a potential that depends on r^2, as with harmonic oscillators, the wave function gets pretty complex pretty fast.

The energy of an isotropic 3D harmonic oscillator is quantized, and you can derive the following relation for the energy levels:

$$E_n = \left(n + \frac{3}{2}\right)\hbar\omega \qquad n = 1, 2, 3\ldots$$

So the energy levels start at $3\hbar\omega/2$ and then go to $5\hbar\omega/2$, $7\hbar\omega/2$, and so on.

Chapter 9

Understanding Hydrogen Atoms

• •

In This Chapter

▶ The Schrödinger equation for hydrogen

▶ The radial wave functions

▶ Energy degeneracy

▶ Location of the electron

• •

*N*ot only is hydrogen the most common element in the universe, but it's also the simplest. And one thing quantum physics is good at is predicting everything about simple atoms. This chapter is all about the hydrogen atom and solving the Schrödinger equation to find the energy levels of the hydrogen atom. For such a small little guy, the hydrogen atom can whip up a lot of math — and I solve that math in this chapter.

Using the Schrödinger equation tells you just about all you need to know about the hydrogen atom, and it's all based on a single assumption: that the wave function must go to zero as r goes to infinity, which is what makes solving the Schrödinger equation possible. I start by introducing the Schrödinger equation for the hydrogen atom and take you through calculating energy degeneracy and figuring out how far the electron is from the proton.

Coming to Terms: The Schrödinger Equation for the Hydrogen Atom

Hydrogen atoms are composed of a single proton, around which rotates a single electron. You can see how that looks in Figure 9-1.

REMEMBER

Note that the proton isn't at the exact center of the atom — the center of mass is at the exact center. In fact, the proton is at a radius of r_p from the exact center, and the electron is at a radius of r_e.
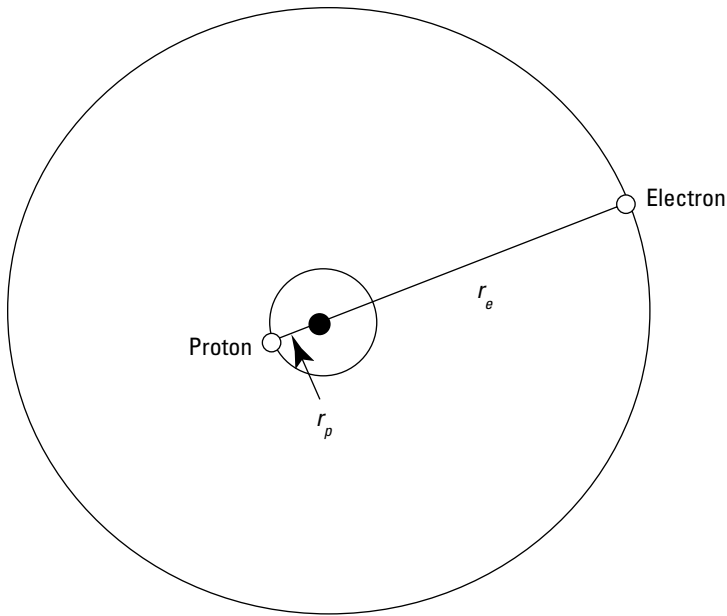
Figure 9-1:
The hydro-
gen atom.

So what does the Schrödinger equation, which will give you the wave equations you need, look like? Well, it includes terms for the kinetic and potential energy of the proton and the electron. Here's the term for the proton's kinetic energy:

$$\frac{-\hbar^2}{2m_p}\nabla_p{}^2$$

where $\nabla_p{}^2 = \frac{\partial^2}{\partial x_p{}^2} + \frac{\partial^2}{\partial y_p{}^2} + \frac{\partial^2}{\partial z_p{}^2}$. Here, x_p is the proton's x position, y_p is the proton's y position, and z_p is its z position.

The Schrödinger equation also includes a term for the electron's kinetic energy:

$$\frac{-\hbar^2}{2m_e}\nabla_e{}^2$$

where $\nabla_e{}^2 = \frac{\partial^2}{\partial x_e{}^2} + \frac{\partial^2}{\partial y_e{}^2} + \frac{\partial^2}{\partial z_e{}^2}$. Here, x_e is the electron's x position, y_e is the electron's y position, and z_e is its z position.

Besides the kinetic energy, you have to include the potential energy, V(*r*), in the Schrödinger equation, which makes the time-independent Schrödinger equation look like this:

$$\frac{-\hbar^2}{2m_p}\nabla_p^{\,2}\psi\left(r_e,r_p\right)-\frac{\hbar^2}{2m_e}\nabla_e^{\,2}\psi\left(r_e,r_p\right)+V\left(r\right)\psi\left(r_e,r_p\right)=E\psi\left(r_e,r_p\right)$$

where ψ(*r*$_e$, *r*$_p$) is the electron and proton's wave function.

The electrostatic potential energy, V(*r*), for a central potential is given by the following formula, where *r* is the radius vector separating the two charges:

$$V\left(r\right)=-\frac{1}{4\pi\varepsilon_0}\frac{e^2}{\left|r\right|}$$

As is common in quantum mechanics, you use CGS (centimeter-gram-second) system of units, where $1=\dfrac{1}{4\pi\varepsilon_0}$.

So the potential due to the electron and proton charges in the hydrogen atom is

$$V\left(r\right)=\frac{-e^2}{\left|r\right|}$$

Note that *r* = *r*$_e$ – *r*$_p$, so the preceding equation becomes

$$V\left(r\right)=\frac{-e^2}{\left|r_e-r_p\right|}$$

which gives you this Schrödinger equation:

$$\frac{-\hbar^2}{2m_p}\nabla_p^{\,2}\psi\left(r_e,r_p\right)-\frac{\hbar^2}{2m_e}\nabla_e^{\,2}\psi\left(r_e,r_p\right)-\frac{e^2}{\left|r_e-r_p\right|}\psi\left(r_e,r_p\right)=E\psi\left(r_e,r_p\right)$$

Okay, so how do you handle this equation? Find out in the next section.

Simplifying and Splitting the Schrödinger Equation for Hydrogen

Here's the usual quantum mechanical Schrödinger equation for the hydrogen atom:

$$\frac{-\hbar^2}{2m_p}\nabla_p^2\psi(\pmb{r}_e,\pmb{r}_p)-\frac{\hbar^2}{2m_e}\nabla_e^2\psi(\pmb{r}_e,\pmb{r}_p)-\frac{e^2}{|\pmb{r}_e-\pmb{r}_p|}\psi(\pmb{r}_e,\pmb{r}_p)=\mathrm{E}\psi(\pmb{r}_e,\pmb{r}_p)$$

The problem is that you're taking into account the distance the proton is from the center of mass of the atom, so the math is messy. If you were to assume that the proton is stationary and that $\pmb{r}_p = 0$, this equation would break down to the following, which is much easier to solve:

$$\frac{-\hbar^2}{2m_e}\nabla_e^2\psi(\pmb{r}_e)-\frac{e^2}{|\pmb{r}_e|}\psi(\pmb{r}_e)=\mathrm{E}\psi(\pmb{r}_e)$$

Unfortunately, that equation isn't exact because it ignores the movement of the proton, so you see the more-complete version of the equation in quantum mechanics texts.

To simplify the usual Schrödinger equation, you switch to center-of-mass coordinates. The center of mass of the proton/electron system is at this location:

$$\pmb{R}=\frac{m_e\pmb{r}_e+m_p\pmb{r}_p}{m_e+m_p}$$

And the vector between the electron and proton is

$$\pmb{r}=\pmb{r}_e-\pmb{r}_p$$

Using vectors $\pmb{R}$ and $\pmb{r}$ instead of $\pmb{r}_e$ and $\pmb{r}_p$ makes the Schrödinger equation easier to solve. The Laplacian for $\pmb{R}$ is $\nabla_{\pmb{R}}^2=\frac{\partial^2}{\partial\mathrm{X}^2}+\frac{\partial^2}{\partial\mathrm{Y}^2}+\frac{\partial^2}{\partial\mathrm{Z}^2}$. And the Laplacian for $\pmb{r}$ is $\nabla_r^2=\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}$.

How can you relate $\nabla_{\pmb{R}}^2$ and ∇_r^2 to the usual equation's ∇_p^2 and ∇_e^2? After the algebra settles, you get

$$\frac{1}{m_e}\nabla_e^2+\frac{1}{m_p}\nabla_p^2=\frac{1}{\mathrm{M}}\nabla_{\pmb{R}}^2+\frac{1}{m}\nabla_r^2$$

where M = m_e + m_p is the total mass and $m = \dfrac{m_e m_p}{m_e + m_p}$ is called the *reduced*

mass. When you put together the equations for the center of mass, the vector between the proton and the electron, the total mass, and *m,* then the time-independent Schrödinger equation becomes the following:

$$\frac{-\hbar^2}{2M}\nabla_R^2\psi(\boldsymbol{R},\boldsymbol{r})-\frac{\hbar^2}{2m}\nabla_r^2\psi(\boldsymbol{R},\boldsymbol{r})+V(\boldsymbol{R},\boldsymbol{r})\psi(\boldsymbol{R},\boldsymbol{r})=E\psi(\boldsymbol{R},\boldsymbol{r})$$

Then, given the vectors, $\boldsymbol{R}$ and $\boldsymbol{r}$, the potential is given by,

$$V(\boldsymbol{R},\boldsymbol{r})=V(\boldsymbol{r})=\frac{-e^2}{|\boldsymbol{r}|}$$

The Schrödinger equation then becomes

$$\frac{-\hbar^2}{2M}\nabla_R^2\psi(\boldsymbol{R},\boldsymbol{r})-\frac{\hbar^2}{2m}\nabla_r^2\psi(\boldsymbol{R},\boldsymbol{r})-\frac{e^2}{|\boldsymbol{r}|}\psi(\boldsymbol{R},\boldsymbol{r})=E\psi(\boldsymbol{R},\boldsymbol{r})$$

This looks easier — the main improvement being that you now have $|\boldsymbol{r}|$ in the denominator of the potential energy term rather than $|\boldsymbol{r}_e - \boldsymbol{r}_p|$.

Because the equation contains terms involving either **R** or *r* but not both, the form of this equation indicates that it's a separable differential equation. And that means you can look for a solution of the following form:

ψ(**R**, *r*) = ψ(**R**)ψ(*r*)

Substituting the preceding equation into the one before it gives you the following:

$$\frac{-\hbar^2}{2M}\nabla_R^2\psi(\mathbf{R})\psi(\boldsymbol{r})-\frac{\hbar^2}{2m}\nabla_r^2\psi(\mathbf{R})\psi(\boldsymbol{r})-\frac{e^2}{|\boldsymbol{r}|}\psi(\mathbf{R})\psi(\boldsymbol{r})=E\psi(\mathbf{R})\psi(\boldsymbol{r})$$

And dividing this equation by ψ(**R**)ψ(*r*) gives you

$$\frac{-\hbar^2}{2M\psi(\mathbf{R})}\nabla_R^2\psi(\mathbf{R})-\frac{\hbar^2}{2m\psi(\boldsymbol{r})}\nabla_r^2\psi(\boldsymbol{r})-\frac{e^2}{|\boldsymbol{r}|}=E$$

Well, well, well. This equation has terms that depend on either $\psi(\mathbf{R})$ or $\psi(\mathbf{r})$ but not both. That means you can separate this equation into *two* equations, like this (where the total energy, E, equals $E_R + E_r$):

> ✔ $\dfrac{-\hbar^2}{2M\psi(\mathbf{R})}\nabla_R^2\psi(\mathbf{R}) = E_R$

> ✔ $\dfrac{-\hbar^2}{2m\psi(\mathbf{r})}\nabla_r^2\psi(\mathbf{r}) - \dfrac{e^2}{|\mathbf{r}|} = E_r$

Multiplying $\dfrac{-\hbar^2}{2M\psi(\mathbf{R})}\nabla_R^2\psi(\mathbf{R}) = E_R$ by $\psi(\mathbf{R})$ gives you

$$\dfrac{-\hbar^2}{2M}\nabla_R^2\psi(\mathbf{R}) = E_R\psi(\mathbf{R})$$

And multiplying $\dfrac{-\hbar^2}{2m\psi(\mathbf{r})}\nabla_r^2\psi(\mathbf{r}) - \dfrac{e^2}{|\mathbf{r}|} = E_r$ by $\psi(\mathbf{r})$ gives you

$$\dfrac{-\hbar^2}{2m}\nabla_r^2\psi(\mathbf{r}) - \dfrac{e^2}{|\mathbf{r}|}\psi(\mathbf{r}) = E_r\psi(\mathbf{r})$$

Now you have two Schrödinger equations. The next two sections show you how to solve them independently.

Solving for ψ (R)

In $\dfrac{-\hbar^2}{2M}\nabla_R^2\psi(\mathbf{R}) = E_R\psi(\mathbf{R})$, how do you solve for $\psi(R)$, which is the wave function of the center of mass of the electron/proton system? This is a straightforward differential equation, and the solution is

$$\psi(\mathbf{R}) = Ce^{-i\mathbf{k}\cdot\mathbf{r}}$$

Here, C is a constant and $\mathbf{k}$ is the wave vector, where $|\mathbf{k}| = \dfrac{2ME_R^{1/2}}{\hbar^2}$.

REMEMBER

In practice, E_R is so small that people almost always just ignore $\psi(\mathbf{R})$ — that is, they assume it to be 1. In other words, the real action is in $\psi(\mathbf{r})$, not in $\psi(\mathbf{R})$; $\psi(\mathbf{R})$ is the wave function for the center of mass of the hydrogen atom, and $\psi(\mathbf{r})$ is the wave function for a (fictitious) particle of mass m.

Solving for ψ (r)

The Schrödinger equation for $\psi(\mathbf{r})$ is the wave function for a made-up particle of mass m (in practice, $m \approx m_e$ and $\psi(\mathbf{r})$ is pretty close to $\psi(\mathbf{r_e})$, so the energy, E_r, is pretty close to the electron's energy). Here's the Schrödinger equation for $\psi(\mathbf{r})$:

$$\frac{-\hbar^2}{2m}\nabla_r^2\psi\left(\mathbf{r}\right)-\frac{e^2}{|\mathbf{r}|}\psi\left(\mathbf{r}\right)=E_r\psi\left(\mathbf{r}\right)$$

You can break the solution, $\psi(\mathbf{r})$, into a radial part and an angular part (see Chapter 8):

$$\psi(\mathbf{r}) = R_{nl}(\mathbf{r})Y_{lm}(\theta, \phi)$$

The angular part of $\psi(\mathbf{r})$ is made up of spherical harmonics, $Y_{lm}(\theta, \phi)$, so that part's okay. Now you have to solve for the radial part, $R_{nl}(r)$. Here's what the Schrödinger equation becomes for the radial part:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}\left[r\,R_{nl}\left(r\right)\right]+l\left(l+1\right)\frac{\hbar^2}{2mr^2}r\,R_{nl}\left(r\right)-\frac{e^2}{r}r\,R_{nl}\left(r\right)=E_r r\,R_{nl}\left(r\right)$$

where $r = |\mathbf{r}|$. To solve this equation, you take a look at two cases — where r is very small and where r is very large. Putting them together gives you the rough form of the solution.

Solving the radial Schrödinger equation for small r

For small r, the terms $-\frac{e^2}{r}rR_{nl}\left(r\right)$ and $E_r rR_{nl}\left(r\right)$, in the previous equation, become much smaller than the rest, so we neglect them and write the radial Schrödinger as,

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}\left[r\,R_{nl}\left(r\right)\right]+l\left(l+1\right)\frac{\hbar^2}{2mr^2}r\,R_{nl}\left(r\right)=0$$

And multiplying by $2m/\hbar^2$, you get

$$\frac{-d^2}{dr^2}\left[r\,R_{nl}\left(r\right)\right]+\frac{l\left(l+1\right)}{r^2}r\,R_{nl}\left(r\right)=0$$

The solution to this equation is proportional to

$$R_{nl}(r) \sim Ar^l + Br^{-l-1}$$

Note, however, that $R_{nl}(r)$ must vanish as r goes to zero — but the r^{-l-1} term goes to infinity. And that means that B must be zero, so you have this solution for small r:

$$R_{nl}(r) \sim r^l$$

That takes care of small r. The next section takes a look at very large r.

Solving the radial Schrödinger equation for large r

For very large r, $\dfrac{-\hbar^2}{2m}\nabla_r^2 \psi(r) - \dfrac{e^2}{|r|}\psi(r) = E_r\psi(r)$ becomes

$$\frac{d^2}{dr^2}\left[r R_{nl}(r)\right] + \frac{2mE_r}{\hbar^2} r R_{nl}(r) = 0$$

Because the electron is in a bound state in the hydrogen atom, E < 0; thus, the solution to the preceding equation is proportional to

$$R_{nl}(r) \sim Ae^{-\lambda r} + Be^{\lambda r}$$

where $\lambda = \dfrac{(-2mE_r)^{\frac{1}{2}}}{\hbar}$.

Note that $R_{nl}(r) \sim Ae^{-\lambda r} + Be^{\lambda r}$ diverges as r goes to infinity because of the $Be^{\lambda r}$ term, so B must be equal to zero. That means that $R_{nl}(r) \sim e^{-\lambda r}$. In the next section, you put the solutions for small r and large r together.

You got the power: Putting together the solution for the radial equation

Putting together the solutions for small r and large r (see the preceding sections), the Schrödinger equation gives you a solution to the radial Schrödinger equation of $R_{nl}(r) = r^l f(r)e^{-\lambda r}$, where f($r$) is some as-yet-undetermined function

of r. Your next task is to determine $f(r)$, which you do by substituting this equation into the radial Schrödinger equation, giving you the following:

$$\frac{-\hbar^2}{2m}\frac{d^2}{dr^2}\Big[r\,R_{nl}(r)\Big]+l(l+1)\frac{\hbar^2}{2mr^2}r\,R_{nl}(r)-\frac{e^2}{r}r\,R_{nl}(r)=E_r r\,R_{nl}(r)$$

Performing the substitution gives you the following differential equation:

$$\frac{d^2}{dr^2}f(r)+2\left[\frac{l+1}{r}-\lambda\right]\frac{df(r)}{dr}+2\left[\frac{\dfrac{me^2}{\hbar^2}-\lambda(l+1)}{r}\right]f(r)=0$$

Quite a differential equation, eh? But just sit back and relax — you solve it with a power series, which is a common way of solving differential equations. Here's the power-series form of $f(r)$ to use:

$$f(r)=\sum_{k=0}^{\infty}a_k r^k$$

Substituting the preceding equation into the one before it gives you

$$\sum_{k=0}^{\infty}\left[k(k+2l+1)a_k r^{k-2}+2\left(\frac{me^2}{\hbar^2}-\lambda(k+l+1)\right)a_k r^{k-1}\right]=0$$

Changing the index of the second term from k to $k-1$ gives you

$$\sum_{k=0}^{\infty}\left[k(k+2l+1)a_k r^{k-2}+2\left[\frac{me^2}{\hbar^2}-\lambda(k+l)\right]a_{k-1} r^{k-2}\right]=0$$

Because each term in this series has to be zero, you have

$$k(k+2l+1)a_k r^{k-2}=2\left[\lambda(k+l)-\frac{me^2}{\hbar^2}\right]a_{k-1}r^{k-2}$$

Dividing by r^{k-2} gives you

$$k(k+2l+1)a_k=2\left[\lambda(k+l)-\frac{me^2}{\hbar^2}\right]a_{k-1}$$

This equation gives the recurrence relation of the infinite series,

$\sum_{k=0}^{\infty} \left[k(k+2l+1)a_k r^{k-2} + 2\left(\frac{me^2}{\hbar^2} - \lambda(k+l+1) \right)a_k r^{k-1} \right] = 0$. That is, if you have one coefficient, you can get the next one using this equation. What does that buy you? Well, take a look at the ratio of a_k/a_{k-1}:

$$\frac{a_k}{a_{k-1}} = \frac{2\left[\lambda(k+l) - \frac{me^2}{\hbar^2} \right]}{k(k+2l+1)}$$

Here's what this ratio approaches as k goes to ∞:

$$\lim_{k\to\infty} \frac{a_k}{a_{k-1}} \to \frac{2\lambda}{k}$$

This resembles the expansion for e^x, which is

$$e^{2x} = \sum_{k=0}^{\infty} \left[\frac{(2x)^k}{k!} \right]^2$$

As for e^{2x}, the ratio of successive terms is

$$\frac{(2x)^k}{k!} \frac{(k-1)!}{(2x)^{k-1}}$$

And in the limit $k \to \infty$, the ratio of successive expansion coefficients of e^{2x} approaches $\frac{2}{k}$:

$$\frac{(2x)^k}{k!} \frac{(k-1)!}{(2x)^{k-1}} \to \frac{2}{k}x \qquad k \to \infty$$

That's the case for e^{2x}. For f(r), you have

$$\lim_{k\to\infty} \frac{a_k}{a_{k-1}} \to \frac{2\lambda}{k}$$

Comparing these two equations, it's apparent that

$$f(r) = \sum_{k=0}^{\infty} a_k r^k = e^{2\lambda r}$$

The radial wave function, $R_{nl}(r)$, looks like this:

$$R_{nl}(r) = r^l f(r) e^{-\lambda r}$$

where $\lambda = \dfrac{(-2mE)^{\frac{1}{2}}}{\hbar}$.

Plugging the form you have for $f(r)$, $f(r) = \sum_{k=0}^{\infty} a_k r^k = e^{2\lambda r}$, into $R_{nl}(r) = r^l f(r) e^{-\lambda r}$ gives you the following:

$$R_{nl}(r) = r^l e^{2\lambda r} e^{-\lambda r}$$
$$= r^l e^{\lambda r}$$

Okay, should you be overjoyed? Well, no. Here's what the wave function $\psi(r)$ looks like: $\psi(r) = R_{nl}(r)\, Y_{lm}(\theta, \phi)$. And substituting in your form of $R_{nl}(r)$ from this equation gives you

$$\psi(r) = r^l e^{\lambda r}\, Y_{lm}(\theta, \phi)$$

That looks fine — except that it goes to infinity as r goes to infinity. You expect $\psi(r)$ to go to zero as r goes to infinity, so this version of $R_{nl}(r) = r^l e^{\lambda r}$ is clearly unphysical. In other words, something went wrong somewhere. How can you fix this version of $f(r)$?

Fixing f(r) to keep it finite

You need the solution for the radial equation to go to zero as r goes to infinity. The problem of having $\psi(r)$ go to infinity as r goes to infinity lies in the form you assume for $f(r)$ in the preceding section, which is

$$f(r) = \sum_{k=0}^{\infty} a_k r^k$$

The solution is to say that this series must terminate at a certain index, which you call N. N is called the *radial quantum number*. So this equation becomes the following (note that the summation is now to N, not infinity):

$$f(r) = \sum_{k=0}^{N} a_k r^k$$

For this series to terminate, a_{N+1}, a_{N+2}, a_{N+3}, and so on must all be zero. The recurrence relation for the coefficients a_k is

$$k(k+2l+1)a_k = 2\left[\lambda(k+l) - \frac{me^2}{\hbar^2}\right]a_{k-1}$$

For a_{N+1} to be zero, the factor multiplying a_{k-1} must be zero for $k = N + 1$, which means that

$$2\left[\lambda(k+l) - \frac{me^2}{\hbar^2}\right] = 0$$

Substituting in k = N + 1 gives you $2\left[\lambda(N+l+1) - \frac{me^2}{\hbar^2}\right] = 0$. And dividing by 2 gives you $\lambda(N+l+1) - \frac{me^2}{\hbar^2} = 0$. Making the substitution N + l + 1 $\to$ n, where n is called the *principal quantum number,* gives you

$$n\lambda - \frac{me^2}{\hbar^2} = 0 \quad n = 1,2,3\ldots$$

This is the quantization condition that must be met if the series for f(r) is to be finite, which it must be, physically:

$$f(r) = \sum_{k=0}^{N} a_k r^k$$

Because $\lambda = \dfrac{(-2mE)^{\frac{1}{2}}}{\hbar}$, the equation $n\lambda - \dfrac{me^2}{\hbar^2} = 0$ puts constraints on the allowable values of the energy.

Finding the allowed energies of the hydrogen atom

The quantization condition for $\psi(r)$ to remain finite as r goes to infinity is

$$n\lambda - \frac{me^2}{\hbar^2} = 0 \qquad n = 1,2,3\ldots$$

where $\lambda = \dfrac{(-2mE)^{\frac{1}{2}}}{\hbar}$. Substituting λ into the quantization-condition equation gives you the following:

$$\frac{n(-2m\mathrm{E})^{\frac{1}{2}}}{\hbar} - \frac{me^2}{\hbar^2} = 0 \qquad n = 1,2,3\ldots$$

$$\frac{n(-2m\mathrm{E})^{\frac{1}{2}}}{\hbar} = \frac{me^2}{\hbar^2}$$

Now solve for the energy, E. Squaring both sides of the preceding equation gives you

$$n^2 \frac{(-2m\mathrm{E})}{\hbar^2} = \frac{m^2 e^4}{\hbar^4} \qquad n = 1,2,3\ldots$$

$$-n^2 2\mathrm{E} = \frac{me^4}{\hbar^2}$$

So here's the energy, E (***Note:*** Because E depends on the principal quantum number, I've renamed it E_n):

$$\mathrm{E}_n = \frac{-me^4}{2n^2\hbar^2} \qquad n = 1,2,3\ldots$$

Physicists often write this result in terms of the *Bohr radius* — the orbital radius that Niels Bohr calculated for the electron in a hydrogen atom, r_0. The Bohr radius is $r_0 = \dfrac{\hbar^2}{me^2}$.

And in terms of r_0, here's what E_n equals:

$$\mathrm{E}_n = \frac{-me^4}{2n^2\hbar^2} = \frac{-e^2}{2r_0}\frac{1}{n^2} \qquad n = 1,2,3\ldots$$

The ground state, where $n = 1$, works out to be about E = –13.6 eV.

Notice that this energy is negative because the electron is in a bound state — you'd have to add energy to the electron to free it from the hydrogen atom. Here are the first and second excited states:

- ✔ **First excited state, $n = 2$:** E = –3.4 eV
- ✔ **Second excited state, $n = 3$:** E = –1.5 eV

Okay, now you've used the quantization condition, which is

$$n\lambda - \frac{me^2}{\hbar^2} = 0 \qquad n = 1,2,3\ldots$$

to determine the energy levels of the hydrogen atom.

Getting the form of the radial solution of the Schrödinger equation

In this section, you complete the calculation of the wave functions. Go to the calculation of $R_{nl}(r)$ (see the earlier section titled "You got the power: Putting together the solution for the radial equation"). So far, you know that

$R_{nl}(r) = r^l f(r) e^{-\lambda r}$, where $f(r) = \sum_{k=0}^{N} a_k r^k$. Therefore,

$$R_{nl}(r) = r^l e^{-\lambda r} \sum_{k=0}^{N} a_k r^k$$

In fact, this isn't quite enough; the preceding equation comes from solving the radial Schrödinger equation:

$$\frac{-\hbar^2}{2m} \frac{d^2}{dr^2} r\, R_{nl}(r) + l(l+1)\frac{\hbar^2}{2mr^2} r\, R_{nl}(r) - \frac{e^2}{r} r\, R_{nl}(r) = E_r r\, R_{nl}(r)$$

The solution is only good to a multiplicative constant, so you add such a constant, A_{nl} (which turns out to depend on the principal quantum number n and the angular momentum quantum number l), like this:

$$R_{nl}(r) = A_{nl} r^l e^{-\lambda r} \sum_{k=0}^{N} a_k r^k$$

You find A_{nl} by normalizing $R_{nl}(r)$.

Now try to solve for $R_{nl}(r)$ by just flat-out doing the math. For example, try to find $R_{10}(r)$. In this case, $n = 1$ and $l = 0$. Then, because $N + l + 1 = n$, you have $N = n - l - 1$. So $N = 0$ here. That makes $R_{nl}(r)$ look like this:

$$R_{10}(r) = A_{nl} r^l e^{-\lambda r} \sum_{k=0}^{0} a_k r^k$$

And the summation in this equation is equal to $\sum_{k=0}^{0} a_k r^k = a_0$, so

$$R_{10}(r) = A_{10} r^l e^{-\lambda r} a_0$$

And because $l = 0$, $r^l = 1$, so $R_{10}(r) = A_{10} e^{-\lambda r} a_0$, where $\lambda = \frac{(-2mE)^{\frac{1}{2}}}{\hbar}$. Therefore, you can also write $R_{10}(r) = A_{10} e^{-\lambda r} a_0$ as

$$R_{10}(r) = A_{10} \exp\left(\frac{-r}{nr_0}\right) a_0$$

where r_0 is the Bohr radius. To find A_{10} and a_0, you normalize $\psi_{100}(r, \theta, \phi)$ to 1, which means integrating $|\psi_{100}(r, \theta, \phi)|^2 d^3 r$ over all space and setting the result to 1.

Now $d^3 r = r^2 \sin\theta \, dr \, d\theta \, d\phi$, and integrating the spherical harmonics, such as Y_{00}, over a complete sphere, $\int |Y_{00}|^2 \sin\theta d\theta d\phi$, gives you 1. Therefore, you're left with the radial part to normalize:

$$1 = \int_0^{+\infty} r^2 |R_{10}(r)|^2 \, dr$$

Plugging $R_{10}(r) = A_{10} \exp\left(\frac{-r}{nr_0}\right) a_0$ into $1 = \int_0^{+\infty} r^2 |R_{10}(r)|^2 \, dr$ gives you

$$1 = A_{10}{}^2 a_0{}^2 \int_0^{+\infty} r^2 \exp\left(\frac{-2r}{nr_0}\right) dr$$

You can solve this kind of integral with the following relation:

$$\int_0^{+\infty} x^n \exp(-ax) \, dx = \frac{n!}{a^{n+1}}$$

With this relation, the equation $1 = A_{10}{}^2 a_0{}^2 \int_0^{+\infty} r^2 \exp\left(\frac{-2r}{nr_0}\right) dr$ becomes

$$1 = A_{10}{}^2 a_0{}^2 \int_0^{+\infty} r^2 \exp\left(\frac{-2r}{nr_0}\right) dr = A_{10}{}^2 a_0{}^2 \frac{r_0{}^3}{4}$$

Therefore,

$$A_{10}{}^2 a_0{}^2 \frac{r_0{}^3}{4} = 1$$

$$A_{10}{}^2 a_0{}^2 = \frac{4}{r_0{}^3}$$

$$A_{10} a_0 = \frac{2}{r_0{}^{\frac{3}{2}}}$$

This is a fairly simple result. Because A_{10} is just there to normalize the result, you can set A_{10} to 1 (this wouldn't be the case if $A_{10}{}^2 a_0{}^2 \frac{r_0{}^3}{4} = 1$ involved multiple terms). Therefore, $a_0 = \frac{2}{r_0{}^{\frac{3}{2}}}$. That's fine, and it makes $R_{10}(r)$, which is

$$R_{10}(r) = A_{10} \exp\left(\frac{-r}{nr_0}\right) a_0$$

$$R_{10}(r) = \frac{2}{r_0{}^{\frac{3}{2}}} e^{\frac{-r}{r_0}}$$

You know that $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r) \, Y_{lm}(\theta, \phi)$.

And so $\psi_{100}(r, \theta, \phi)$ becomes

$$\psi_{100}(r,\theta,\phi) = \frac{2}{r_0^{\frac{3}{2}}} e^{\frac{-r}{r_0}} Y_{00}(\theta,\phi)$$

Whew. In general, here's what the wave function $\psi_{nlm}(r, \theta, \phi)$ looks like for hydrogen:

$$\psi_{nlm}(r,\theta,\phi) = \frac{\left(\frac{2}{nr_0}\right)^{\frac{3}{2}} \left[(n-l-1)!\right]^{\frac{1}{2}}}{\left[2n(n-1)!\right]^{\frac{1}{2}}} e^{\frac{-r}{nr_0}} \left(\frac{2r}{nr_0}\right)^l L_{n-l-1}^{2l+1}\left(\frac{2r}{nr_0}\right) Y_{lm}(\theta,\phi)$$

where $L_{n-l-1}^{2l+1}(2r/nr_0)$ is a generalized Laguerre polynomial. Here are the first few generalized Laguerre polynomials:

- $L_0^b(r) = 1$
- $L_1^b(r) = -r + b + 1$
- $L_2^b(r) = \frac{r^2}{2} - (b+2)r + \frac{(b+2)(b+1)}{2}$
- $L_3^b(r) = -\frac{r^3}{6} + \frac{(b+3)r^2}{2} - \frac{(b+2)(b+3)r}{2} + \frac{(b+1)(b+2)(b+3)}{6}$

Some hydrogen wave functions

So what do the hydrogen wave functions look like? In the preceding section, you find that $\psi_{100}(r, \theta, \phi)$ looks like this:

$$\psi_{100}(r,\theta,\phi) = \frac{2}{r_0^{\frac{3}{2}}} e^{\frac{-r}{r_0}} Y_{00}(\theta,\phi)$$

Here are some other hydrogen wave functions:

- $\psi_{20m}(r,\theta,\phi) = \frac{1}{2^{\frac{1}{2}}} \frac{1}{r_0^{\frac{3}{2}}} \left(1 - \frac{r}{2r_0}\right) e^{-\frac{r}{2r_0}} Y_{0m}(\theta,\phi)$

- $\psi_{21m}(r,\theta,\phi) = \frac{1}{6^{\frac{1}{2}} r_0^{\frac{3}{2}}} \frac{r}{2r_0} e^{\frac{-r}{2r_0}} Y_{1m}(\theta,\phi)$

$$\checkmark \; \psi_{300}(r,\theta,\phi) = \frac{2}{3\left(3^{\frac{1}{2}}\right)r_0^{\frac{3}{2}}} e^{\frac{-r}{3r_0}}\left[1 - \left(\frac{2r}{3r_0}\right) + \left(\frac{2r^2}{27r_0^2}\right)\right]Y_{00}(\theta,\phi)$$

$$\checkmark \; \psi_{31m}(r,\theta,\phi) = \frac{8}{9\left(6^{\frac{1}{2}}\right)r_0^{\frac{3}{2}}} e^{\frac{-r}{3r_0}}\frac{r}{3r_0}\left[1 - \left(\frac{r}{6r_0}\right)\right]Y_{1m}(\theta,\phi)$$

$$\checkmark \; \psi_{32m}(r,\theta,\phi) = \frac{4}{9(30)^{\frac{1}{2}}r_0^{\frac{3}{2}}}\frac{r^2}{9r_0^2} e^{\frac{-r}{3r_0}}Y_{2m}(\theta,\phi)$$

Note that $\psi_{nlm}(r, \theta, \phi)$ behaves like r^l for small r and therefore goes to zero. And for large r, $\psi_{nlm}(r, \theta, \phi)$ decays exponentially to zero. So you've solved the problem you had earlier of the wave function diverging as r becomes large — and all because of the quantization condition, which cut the expression for f(r) from an exponent to a polynomial of limited order. Not bad.

You can see the radial wave function $R_{10}(r)$ in Figure 9-2. $R_{20}(r)$ appears in Figure 9-3. And you can see $R_{21}(r)$ in Figure 9-4.
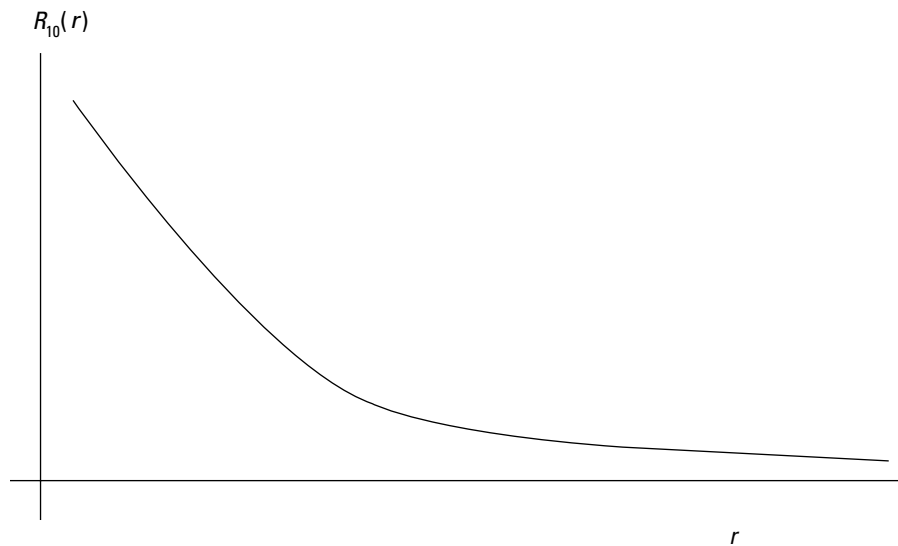

Figure 9-2:
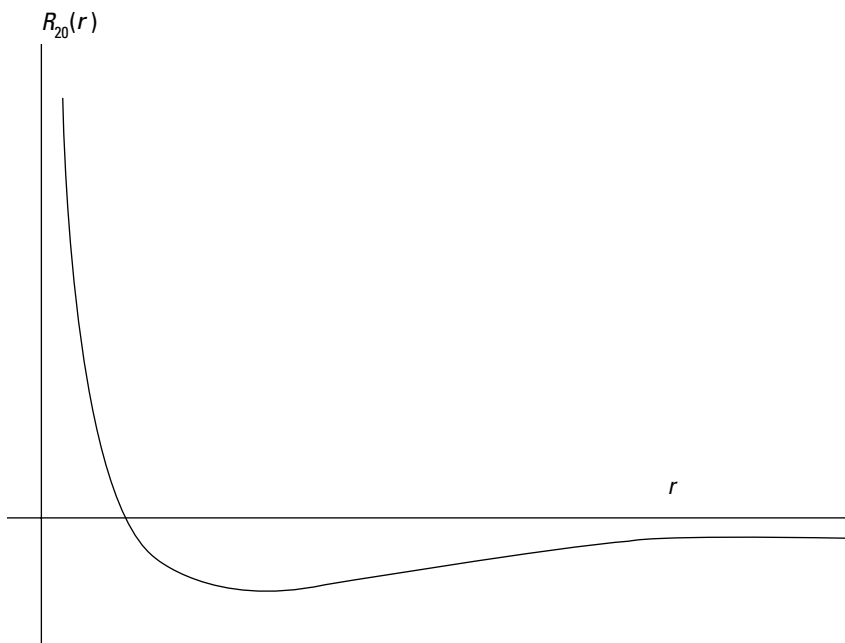The radial wave function $R_{10}(r)$.

$R_{20}(r)$

r

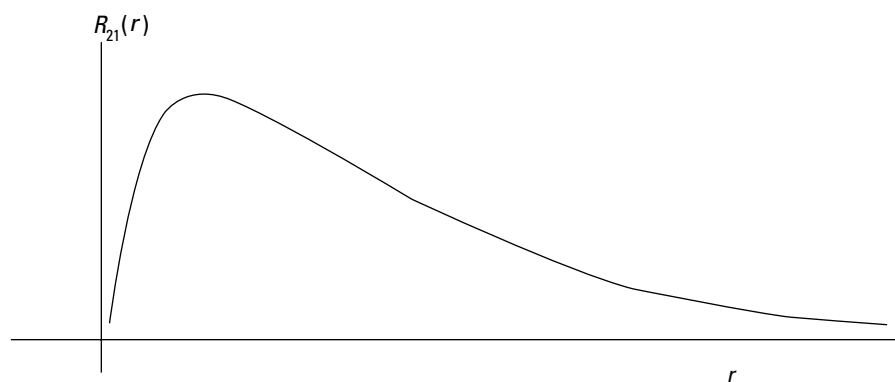**Figure 9-3:**
$R_{20}(r)$.

$R_{21}(r)$

r

Figure 9-4:
$R_{21}(r)$.

Calculating the Energy Degeneracy of the Hydrogen Atom

Each quantum state of the hydrogen atom is specified with three quantum numbers: n (the principal quantum number), l (the angular momentum quantum number of the electron), and m (the z component of the electron's

angular momentum, $\psi_{nlm}[r, \theta, \phi]$). How many of these states have the same energy? In other words, what's the energy degeneracy of the hydrogen atom in terms of the quantum numbers n, l, and m?

Well, the actual energy is just dependent on n, as you see earlier in the section titled "Finding the allowed energies of the hydrogen atom":

$$E_n = \frac{-me^4}{2n^2\hbar^2} \quad n = 1,2,3\ldots$$

where m is the mass, not the quantum number. That means the E is independent of l and m. So how many states, $|n, l, m>$, have the same energy for a particular value of n? Well, for a particular value of n, l can range from zero to $n - 1$. And each l can have different values of m, so the total degeneracy is

$$\text{Degeneracy} = \sum_{l=0}^{n-1} \left(\text{Degeneracy in } m \right)$$

The degeneracy in m is the number of states with different values of m that have the same value of l. For any particular value of l, you can have m values of $-l, -l + 1, \ldots, 0, \ldots, l - 1, l$. And that's $(2l + 1)$ possible m states for a particular value of l. So you can plug in $(2l + 1)$ for the degeneracy in m:

$$\text{Degeneracy} = \sum_{l=0}^{n-1} \left(2l + 1 \right)$$

And this series works out to be just n^2.

So the degeneracy of the energy levels of the hydrogen atom is n^2. For example, the ground state, $n = 1$, has *degeneracy* = n^2 = 1 (which makes sense because l, and therefore m, can only equal zero for this state).

For $n = 2$, you have a degeneracy of 4:

- ✔ $\psi_{200}(r, \theta, \phi)$
- ✔ $\psi_{21-1}(r, \theta, \phi)$
- ✔ $\psi_{210}(r, \theta, \phi)$
- ✔ $\psi_{211}(r, \theta, \phi)$

Cool.

Quantum states: Adding a little spin

You may be asking yourself — what about the spin of the electron? Right you are! The spin of the electron does provide additional quantum states. Up to now in this section, you've been treating the wave function of the hydrogen atom as a product of radial and angular parts:

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$$

Now you can add a spin part, corresponding to the spin of the electron, where s is the spin of the electron and m_s is the z component of the spin:

$$\left|s, m_s\right\rangle$$

The spin part of the equation can take the following values:

- ✔ $|^1/_2, \, ^1/_2>$
- ✔ $|^1/_2, \, -^1/_2>$

Hence, $\psi_{nlm}(r, \theta, \phi)$ now becomes $\psi_{nlmm_s}(r, \theta, \phi)$:

$$\psi_{nlmm_s}\left(r, \theta, \phi\right) = R_{nl}\left(r\right)Y_{lm}\left(\theta, \phi\right)\left|s, m_s\right\rangle$$

And this wave function can take two different forms, depending on m_s, like this:

- ✔ $\psi_{nlm\frac{1}{2}}\left(r, s, \theta, \phi\right) = R_{nl}\left(r\right)Y_{lm}\left(\theta, \phi\right)\left|\frac{1}{2}, \frac{1}{2}\right\rangle$
- ✔ $\psi_{nlm-\frac{1}{2}}\left(r, s, \theta, \phi\right) = R_{nl}\left(r\right)Y_{lm}\left(\theta, \phi\right)\left|\frac{1}{2}, -\frac{1}{2}\right\rangle$

In fact, you can use the spin notation (which you use in Chapter 6), where

$$\left|\frac{1}{2}, \frac{1}{2}\right\rangle = \begin{bmatrix} 1 \\ 0 \end{bmatrix}$$

$$\left|\frac{1}{2}, -\frac{1}{2}\right\rangle = \begin{bmatrix} 0 \\ 1 \end{bmatrix}$$

For example, for $|^1/_2, {}^1/_2>$, you can write the wave function as

$$\psi_{nlm\frac{1}{2}}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)\begin{bmatrix} 1 \\ 0 \end{bmatrix} = \begin{bmatrix} \psi_{nlm}(r,\theta,\phi) \\ 0 \end{bmatrix}$$

And for $|^1/_2, -^1/_2>$, you can write the wave function as

$$\psi_{nlm-\frac{1}{2}}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)\begin{bmatrix} 0 \\ 1 \end{bmatrix} = \begin{bmatrix} 0 \\ \psi_{nlm}(r,\theta,\phi) \end{bmatrix}$$

What does this do to the energy degeneracy? If you include the spin of the electron, there are two spin states for every state $|n, l, m>$, so the degeneracy becomes

$$\text{Degeneracy} = \sum_{l=0}^{n-1} 2(2l+1) = 2n^2$$

So if you include the electron's spin, the energy degeneracy of the hydrogen atom is $2n^2$.

In fact, you can even add the spin of the proton to the wave function (although people don't usually do that, because the proton's spin interacts only weakly with magnetic fields applied to the hydrogen atom). In that case, you have a wave function that looks like the following:

$$\psi_{nlmm_{se}m_{sp}}(r,\theta,\phi) = R_{nl}(r)Y_{lm}(\theta,\phi)|s_e,m_{se}\rangle|s_p,m_{sp}\rangle$$

where s_e is the spin of the electron, m_{se} is the z component of the electron's spin, s_p is the spin of the proton, and m_{sp} is the z component of the proton's spin.

If you include the proton's spin, the wave function can now take four different forms, depending on m_s, like this:

- $\psi_{nlm\frac{1}{2}\frac{1}{2}}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) \left| \frac{1}{2}, \frac{1}{2} \right\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle$

- $\psi_{nlm\frac{1}{2}-\frac{1}{2}}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) \left| \frac{1}{2}, \frac{1}{2} \right\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$

- $\psi_{nlm-\frac{1}{2}\frac{1}{2}}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \left| \frac{1}{2}, \frac{1}{2} \right\rangle$

- $\psi_{nlm-\frac{1}{2}-\frac{1}{2}}(r,\theta,\phi) = R_{nl}(r) Y_{lm}(\theta,\phi) \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \left| \frac{1}{2}, -\frac{1}{2} \right\rangle$

The degeneracy must now include the proton's spin, so that's a factor of four for each |*n, l, m*>:

$$\text{Degeneracy} = \sum_{l=0}^{n-1} 4(2l+1)$$

$$= 4n^2$$

On the lines: Getting the orbitals

When you study heated hydrogen in spectroscopy, you get a spectrum consisting of various lines, named the *s* (for *sharp*), *p* (for *principal*), *d* (for *diffuse*), and *f* (for *fundamental*) lines. And other, unnamed lines are present as well — the *g, h,* and so on.

The *s, p, d, f,* and the rest of the lines turn out to correspond to different angular momentum states of the electron, called *orbitals.* The *s* state corresponds to *l* = 0; the *p* state, to *l* = 1; the *d* state, to *l* = 2; the *f* state, to *l* = 3; and so on. Each of these angular momentum states has a differently shaped electron cloud around the proton — that is, a different orbital.

Three quantum numbers — *n, l,* and *m* — determine orbitals. For example, the electron cloud for the |1, 0, 0> state (1*s*, with *m* = 0) appears in Figure 9-5.
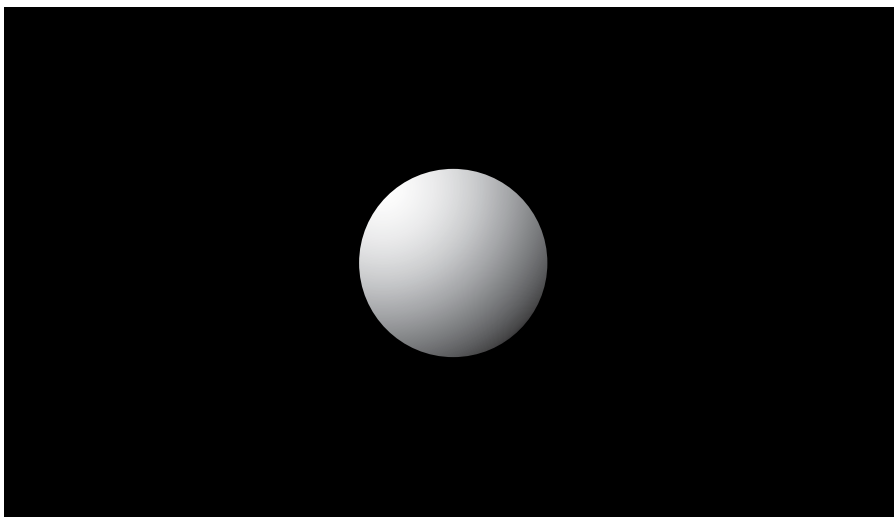
Figure 9-5:
The |1, 0, 0>
state.

The |3, 2, 1> state (3*d,* with *m* = 2) appears in Figure 9-6.

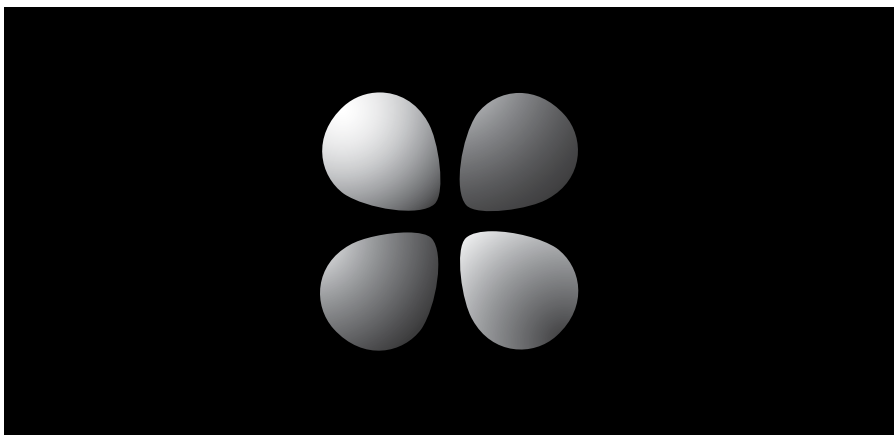**Figure 9-6:**
The |3, 2, 1>
state.

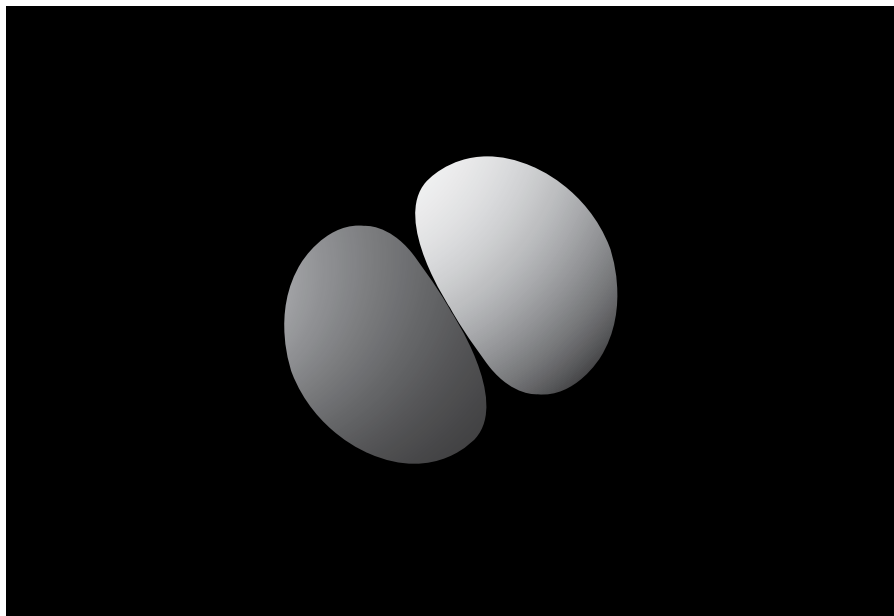The $|2, 1, 1>$ state ($2p$, with $m = 1$) appears in Figure 9-7.

Figure 9-7:
The $|2, 1, 1>$
state.

Hunting the Elusive Electron

Just where is the electron at any one time? In other words, how far is the electron from the proton? You can find the expectation value of r, that is, $<r>$, to tell you. If the wave function is $\psi_{nlm}(r, \theta, \phi)$, then the following expression represents the probability that the electron will be found in the spatial element d^3r:

$$|\psi_{nlm}(r, \theta, \phi)|^2 d^3r$$

In spherical coordinates, $d^3r = r^2 \sin\theta \, dr \, d\theta \, d\phi$. So you can write $|\psi_{nlm}(r, \theta, \phi)|^2 d^3r$ as

$$|\psi_{nlm}(r, \theta, \phi)|^2 r^2 \sin\theta \, dr \, d\theta \, d\phi$$

The probability that the electron is in a spherical shell of radius r to $r + dr$ is therefore

$$\int_0^{2\pi} \int_0^{\pi} |\psi_{nlm}(r,\theta,\phi)|^2 r^2 \sin\theta \, d\theta \, d\phi \, dr$$

And because $\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi)$, this equation becomes the following:

$$\int_0^{2\pi}\int_0^\pi \left|R_{nl}(r)Y_{lm}(\theta,\phi)\right|^2 r^2 \sin\theta\, d\theta\, d\phi\, dr$$

The preceding equation is equal to

$$\left|R_{nl}(r)\right|^2 r^2 dr \int_0^\pi \left|Y_{lm}(\theta,\phi)\right|^2 \sin\theta\, d\theta \int_0^{2\pi} d\phi$$

$$\text{or } \left|R_{nl}(r)\right|^2 r^2 dr \int_0^\pi Y_{lm}{}^*(\theta,\phi)Y_{lm}(\theta,\phi)\sin\theta\, d\theta \int_0^{2\pi} d\phi$$

Spherical harmonics are normalized, so this just becomes

$$\left|R_{nl}(r)\right|^2 r^2\, dr$$

Okay, that's the probability that the electron is inside the spherical shell from r to $r + dr$. So the expectation value of r, which is <r>, is

$$\langle r \rangle = \int_0^\infty r\left|R_{nl}(r)\right|^2 r^2\, dr$$

which is

$$\langle r \rangle = \int_0^\infty r^3 \left|R_{nl}(r)\right|^2 dr$$

This is where things get more complex, because $R_{nl}(r)$ involves the Laguerre polynomials. But after a lot of math, here's what you get:

$$\langle r \rangle = \int_0^\infty r^3 \left|R_{nl}(r)\right|^2 dr = \left[3n^2 - l(l+1)\right]\frac{r_0}{2}$$

where r_0 is the Bohr radius: $r_0 = \dfrac{\hbar^2}{me^2}$. The Bohr radius is about 5.29×10^{-11} meters, so the expectation value of the electron's distance from the proton is

$$<r> = [3n^2 - l(l+1)](2.65 \times 10^{-11}) \text{ meters}$$

So, for example, in the 1s state ($|1, 0, 0\rangle$), the expectation value of r is equal to

$$\langle r \rangle_{1s} = 3(2.65 \times 10^{-11}) = 7.95 \times 10^{-11} \text{ meters}$$

And in the 4p state ($|4, 1, m\rangle$),

$$\langle r \rangle_{4p} = 46(2.65 \times 10^{-11}) = 1.22 \times 10^{-9} \text{ meters}$$

And that concludes this chapter, which has been a triumph for the Schrödinger equation.

Chapter 10

Handling Many Identical Particles

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*H*ydrogen atoms (see Chapter 9) involve only a proton and an electron, but all other atoms involve more electrons than that. So how do you deal with multiple-electron atoms? For that matter, how do you deal with multi-particle systems, such as even a simple gas?

In general, you *can't* deal with problems like this — exactly, anyway. Imagine the complexity of just two electrons moving in a helium atom — you'd have to take into account the interaction of the electrons not only with the nucleus of the atom but also with each other — and that depends on their relative positions. So not only does the Hamiltonian have a term in $1/r_1$ for the potential energy of the first electron and $1/r_2$ for the second electron, but it also has

a term in $-\dfrac{1}{|r_1 - r_2|}$ for the potential energy that comes from the interaction of

the two electrons. And that makes an exact wave function just about impossible to find.

However, even without finding exact wave functions, you can still do a surprising amount with multi-particle systems, such as deriving the *Pauli exclusion principle* — which says, among other things, that no two electrons can be in the exact same quantum state. In fact, you'll probably be surprised at how much you can actually say about multi-particle systems using quantum mechanics. This chapter starts with an introduction to many-particle systems and goes on to discuss identical particles, symmetry (and anti-symmetry), and electron shells.

Many-Particle Systems, Generally Speaking

You can see a multi-particle system in Figure 10-1, where a number of particles are identified by their position (ignore spin for the moment). This section explains how to describe that system in quantum physics terms.
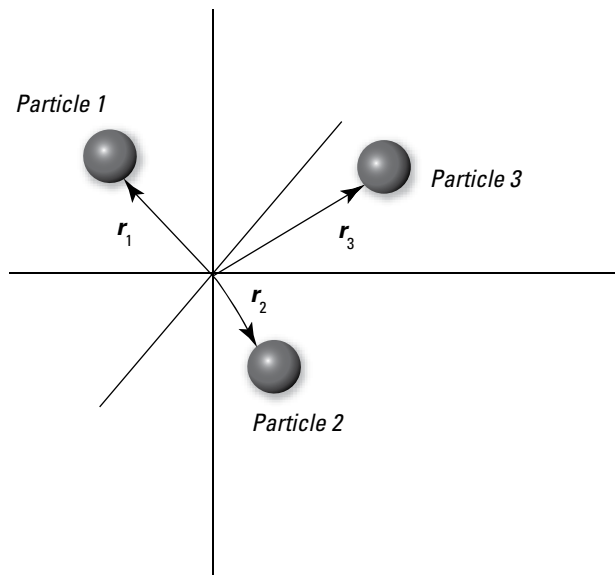
Considering wave functions and Hamiltonians

Begin by working with the wave function. The state of a system with many particles, as shown in Figure 10-1, is given by $\psi(r_1, r_2, r_3, ...)$. And here's the probability that particle 1 is in $d^3 r_1$, particle 2 is in $d^3 r_2$, particle 3 is in $d^3 r_3$, and so on:

$$\left| \psi\left(r_1, r_2, r_3, \ldots\right) \right|^2 d^3 r_1 d^3 r_2 d^3 r_3 \ldots$$

The normalization of $\psi(r_1, r_2, r_3, ...)$ demands that

$$\int_{-\infty}^{+\infty} \left| \psi\left(r_1, r_2, r_3, \ldots\right) \right|^2 d^3 r_1 d^3 r_2 d^3 r_3 \ldots = 1$$

Okay, so what about the Hamiltonian, which gives you the energy states? That is, what is H, where Hψ(r_1, r_2, r_3, ...) = Eψ(r_1, r_2, r_3, ...)? When you're dealing with a single particle, you can write this as

$$\frac{p^2}{2m}\psi(\boldsymbol{r}) + V(\boldsymbol{r})\psi(\boldsymbol{r}) = E\psi(\boldsymbol{r})$$

But in a many particle system the Hamiltonian must represent the total energy of all particles, not just one.

The total energy of the system is the sum of the energy of all the particles (omitting spin for the moment), so here's how you can generalize the Hamiltonian for multi-particle systems:

$$H\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...) = \sum_{i=1}^{N}\frac{p_i^2}{2m_i}\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...) + V(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...)\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...)$$

This, in turn, equals the following:

$$H\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...) = \sum_{i=1}^{N}\frac{p_i^2}{2m_i}\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...) + V(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...)\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...)$$

$$= \sum_{i=1}^{N}\frac{-\hbar^2}{2m_i}\nabla_i^2\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...) + V(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...)\psi(\boldsymbol{r}_1,\boldsymbol{r}_2,\boldsymbol{r}_3,...)$$

Here, m_i is the mass of the ith particle and V is the multi-particle potential.

A Nobel opportunity: Considering multi-electron atoms

This section takes a look at how the Hamiltonian wave function (see the preceding section) would work for a neutral, multi-electron atom. A multi-electron atom, which you see in Figure 10-2, is the most common multi-particle system that quantum physics considers. Here, **R** is the coordinate of the nucleus (relative to the center of mass), r_1 is the coordinate of the first electron (relative to the center of mass), r_2 the coordinate of the second electron, and so on.

Figure 10-2:
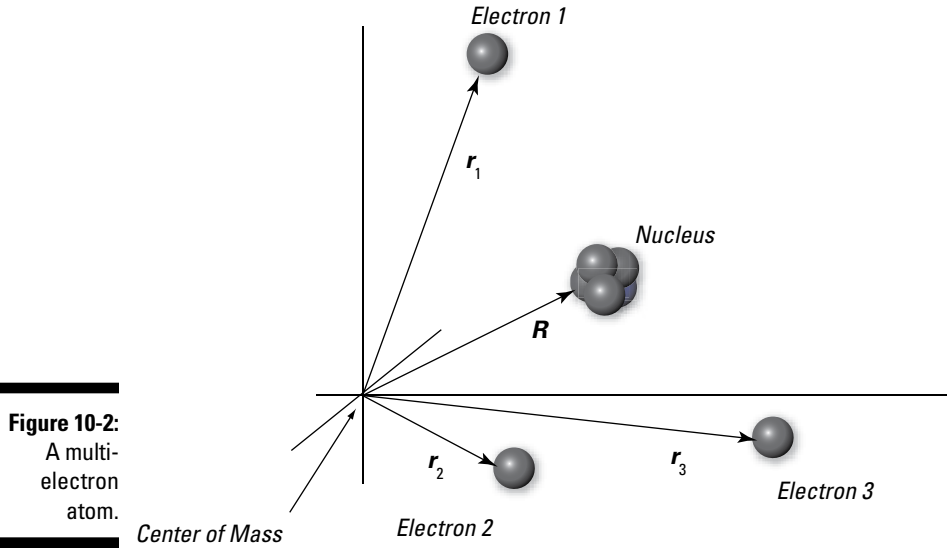A multi-
electron
atom.

If you have Z electrons, the wave function looks like $\psi(r_1, r_2, ..., r_Z, R)$. And the kinetic energy of the electrons and the nucleus looks like this:

$$KE = \sum_{i=1}^{Z} \frac{-\hbar^2}{2m_i} \nabla_i^2 \psi(r_1, r_2, ... r_Z, R) - \frac{\hbar^2}{2M} \nabla_R^2 \psi(r_1, r_2, ... r_Z, R)$$

And the potential energy of the system looks like this:

$$PE = -\sum_{i=1}^{Z} \frac{Ze^2}{|r_i - R|} \psi(r_1, r_2, ... r_Z, R) + \sum_{i>j} \frac{e^2}{|r_i - r_j|} \psi(r_1, r_2, ... r_Z, R)$$

So adding the two preceding equations, here's what you get for the total energy (E = KE + PE) of a multi-particle atom:

$$E\psi(r_1, r_2, ... r_Z, R) = \sum_{i=1}^{Z} \frac{-\hbar^2}{2m_i} \nabla_i^2 \psi(r_1, r_2, ... r_Z, R) - \frac{\hbar^2}{2M} \nabla_R^2 \psi(r_1, r_2, ... r_Z, R)$$
$$- \sum_{i=1}^{Z} \frac{Ze^2}{|r_i - R|} \psi(r_1, r_2, ... r_Z, R) + \sum_{i>j} \frac{e^2}{|r_i - r_j|} \psi(r_1, r_2, ... r_Z, R)$$

Okay, now that looks like a proper mess. Want to win the Nobel prize in physics? Just come up with the general solution to the preceding equation. As is always the case when you have a multi-particle system in which the particles interact with each other, you can't split this equation into a system of N independent equations.

In cases where the N particles of a multi-particle system *don't* interact with each other, where you can disconnect the Schrödinger equation into a set of N independent equations, solutions may be possible. But when the particles interact and the Schrödinger equation depends on those interactions, you can't solve that equation for any significant number of particles.

However, that doesn't mean all is lost by any means. You can still say plenty about equations like this one if you're clever — and it all starts with an examination of the symmetry of the situation, which I discuss next.

A Super-Powerful Tool: Interchange Symmetry

Even though finding general solutions for equations like the one for the total energy of a multi-particle atom (in the preceding section) is impossible, you can still see what happens when you exchange particles with each other — and the results are very revealing. This section covers the idea of interchange symmetry.

Order matters: Swapping particles with the exchange operator

You can determine what happens to the wave function when you swap two particles. Whether the wave function is symmetric under such operations gives you insight into whether two particles can occupy the same quantum state. This section discusses swapping particles and looking at symmetric and antisymmetric functions.

Take a look at the general wave function for N particles:

$$\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N)$$

Note: In this chapter, I talk about symmetry in terms of the location coordinate, *r,* to keep things simple, but you can also consider other quantities, such as spin, velocity, and so on. That wouldn't make this discussion any different, because you can wrap all of a particle's quantum measurements — location, velocity, speed, and so on — into a single quantum state, which you can call ξ. Doing so would make the general wave function for N particles into this: $\psi(\xi_1, \xi_2, ..., \xi_i, ..., \xi_j, ..., \xi_N)$. But as I said, this section just considers the wave function $\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N)$ to keep things simple.

Now imagine that you have an exchange operator, P_{ij}, that exchanges particles i and j. In other words,

$$P_{ij}\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N) = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_N)$$

And $P_{ij} = P_{ji}$, so

$$P_{ij}\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N) = \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_N)$$
$$= P_{ji}\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N)$$

Also, note that applying the exchange operator twice just puts the two exchanged particles back where they were originally, so $P_{ij}^2 = 1$. Here's what that looks like:

$$P_{ij} P_{ij} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N) = P_{ij}\psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_N)$$
$$= \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, ..., \boldsymbol{r}_i, ..., \boldsymbol{r}_j, ..., \boldsymbol{r}_N)$$

However, in general, P_{ij} and P_{lm} (where $ij \neq lm$) do not commute. That is, $P_{ij} P_{lm} \neq P_{lm} P_{ij}$ $(ij \neq lm)$. Therefore, $[P_{ij}, P_{lm}] \neq 0$ $(ij \neq lm)$. For example, say you have four particles whose wave function is

$$\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4\right) = \frac{r_1 r_3}{r_4} e^{r_2}$$

Apply the exchange operators P_{12} and P_{14} to see whether $P_{12} P_{14}$ equals $P_{14} P_{12}$. Here's $P_{14} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$:

$$P_{14}\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4\right) = \frac{r_4 r_3}{r_1} e^{r_2}$$

And here's what $P_{12}P_{14} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$ looks like:

$$P_{12}P_{14}\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4\right) = \frac{r_2 r_3}{r_1} e^{r_4}$$

Okay. Now take a look at $P_{14} P_{12} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$. Here's $P_{12} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$:

$$P_{12}\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4\right) = \frac{r_2 r_3}{r_4} e^{r_1}$$

And here's what $P_{14} P_{12} \psi(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4)$ looks like:

$$P_{14}P_{12}\psi\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \boldsymbol{r}_3, \boldsymbol{r}_4\right) = \frac{r_4 r_3}{r_2} e^{r_1}$$

As you can see by comparing $P_{12}P_{14}\psi(r_1,r_2,r_3,r_4)=\dfrac{r_2r_3}{r_1}e^{r_4}$ and this last equation,

$P_{12}P_{14}\psi(r_1, r_2, r_3, r_4) \neq P_{14}P_{12}\psi(r_1, r_2, r_3, r_4)$. In other words, the order in which you apply exchange operators *matters*.

Classifying symmetric and antisymmetric wave functions

$P_{ij}^2 = 1$ (see the preceding section), so note that if a wave function is an eigenfunction of P_{ij}, then the possible eigenvalues are 1 and –1. That is, for $\psi(r_1, r_2, ..., r_i, ..., r_j, ..., r_N)$ an eigenfunction of P_{ij} looks like

$$P_{ij}\psi(r_1, r_2, ..., r_i, ..., r_j, ..., r_N) = \psi(r_1, r_2, ...r_i, ..., r_j, ..., r_N)$$
$$\text{or} -\psi(r_1, r_2, ..., r_i, ..., r_j, ..., r_N)$$

That means there are two kinds of eigenfunctions of the exchange operator:

✔ **Symmetric eigenfunctions:** $P_{ij}\psi_s(r_1, r_2, ..., r_i, ..., r_j, ..., r_N) = \psi_s(r_1, r_2, ..., r_i, ..., r_j, ..., r_N)$

✔ **Antisymmetric eigenfunctions:** $P_{ij}\psi_a(r_1, r_2, ..., r_i, ..., r_j, ..., r_N) = -\psi_a(r_1, r_2, ..., r_i, ..., r_j, ..., r_N)$

Now take a look at some symmetric and some antisymmetric eigenfunctions. How about this one — is it symmetric or antisymmetric?

$$\psi_1(r_1, r_2) = (r_1 - r_2)^2$$

You can apply the exchange operator P_{12}:

$$P_{12}\psi_1(r_1, r_2) = (r_2 - r_1)^2$$

Note that because $(r_1 - r_2)^2 = (r_2 - r_1)^2$, $\psi_1(r_1, r_2)$ is a symmetric wave function; that's because $P_{12}\psi_1(r_1, r_2) = \psi_1(r_1, r_2)$.

How about this wave function?

$$\psi_2(r_1, r_2) = \frac{r_1^{\,2} + r_2^{\,2}}{(r_1 - r_2)^2}$$

Again, apply the exchange operator, P_{12}:

$$P_{12}\psi_2(r_1, r_2) = \frac{r_2^2 + r_1^2}{(r_2 - r_1)^2}$$

Okay, but because $\dfrac{r_2^{\,2} + r_1^{\,2}}{(r_2 - r_1)^2} = \dfrac{r_1^{\,2} + r_2^{\,2}}{(r_1 - r_2)^2}$, you know that $P_{12}\psi_2(r_1, r_2) = \psi_2(r_1, r_2)$,

so $\psi_2(r_1, r_2)$ is symmetric.

Here's another one:

$$\psi_3(r_1 - r_2) = \frac{5(r_1 - r_2)}{(r_1 - r_2)^2}$$

Now apply P_{12}:

$$P_{12}\psi_3(r_1, r_2) = \frac{5(r_2 - r_1)}{(r_2 - r_1)^2}$$

How does that equation compare to the original one? Well,

$\dfrac{5(r_2 - r_1)}{(r_2 - r_1)^2} = \dfrac{-5(r_1 - r_2)}{(r - r)^2}$, so $P_{12}\psi_3(r_1, r_2) = -\psi_3(r_1, r_2)$). Therefore, $\psi_3(r_1, r_2)$ is

antisymmetric.

What about this one?

$$\psi_4(r_1, r_2) = \frac{r_1 r_2}{(r_1 - r_2)^2} + r_1^{\,2} + r_2^{\,2}$$

To find out, apply P_{12}:

$$P_{12}\psi_4(r_1, r_2) = \frac{r_2 r_1}{(r_2 - r_1)^2} + r_2^{\,2} + r_1^{\,2}$$

All right — how's this compare with the original equation?

$$\frac{r_1 r_2}{(r_1 - r_2)^2} + r_1^{\,2} + r_2^{\,2} = \frac{r_2 r_1}{(r_2 - r_1)^2} + r_2^{\,2} + r_1^{\,2}$$

Okay — $\psi_4(r_1, r_2)$ is symmetric.

You may think you have this process down pretty well, but what about this next wave function?

$$\psi_5\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\frac{r_1 r_2}{\left(r_1-r_2\right)^2}+r_1^{\;2}-r_2^{\;2}$$

Start by applying P_{12}:

$$P_{12}\psi_5\left(\boldsymbol{r}_1,\boldsymbol{r}_2\right)=\frac{r_2 r_1}{\left(r_2-r_1\right)^2}+r_2^2-r_1^2$$

So how do these two equations compare?

$$\frac{r_1 r_2}{\left(r_1-r_2\right)^2}+r_1^{\;2}-r_2^{\;2}\neq\frac{r_2 r_1}{\left(r_2-r_1\right)^2}+r_2^{\;2}-r_1^{\;2}$$

That is, $\psi_5(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is neither symmetric nor antisymmetric. In other words, $\psi_5(\boldsymbol{r}_1,\boldsymbol{r}_2)$ is not an eigenfunction of the P_{12} exchange operator.

Floating Cars: Tackling Systems of Many Distinguishable Particles

All right, if you've been reading this chapter from the start, you pretty much have the idea of swapping particles down. Now you look at systems of particles that you can distinguish — that is, systems of identifiably different particles. As you see in this section, you can decouple such systems into linearly independent equations.

Suppose you have a system of many different types of cars floating around in space. You can distinguish all those cars because they're all different — they have different masses, for one thing.

Now say that each car interacts with its own potential — that is, the potential that any one car sees doesn't depend on any other car. That means that the potential for all cars is just the sum of the individual potentials each car sees, which looks like this, assuming you have N cars:

$$PE=V\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\dots,\boldsymbol{r}_N\right)=\sum_{i=1}^{N}V\left(\boldsymbol{r}_i\right)$$

Being able to cut the potential energy up into a sum of independent terms like this makes life a lot easier. Here's what the Hamiltonian looks like:

$$H\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N\right)=\sum_{i=1}^{N}\left[\frac{-\hbar^2}{2m_i}\nabla_i^2+V_i\left(r_i\right)\right]\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N\right)$$

Notice how much simpler this equation is than the Hamiltonian for the hydrogen atom which I give you here:

$$H\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_Z,\boldsymbol{R}\right)=\quad \sum_{i=1}^{Z}\frac{-\hbar^2}{2m_i}\nabla_i^2\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_Z,\boldsymbol{R}\right)-\frac{\hbar^2}{2M}\nabla_R^2\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_Z,\boldsymbol{R}\right)$$

$$-\sum_{i=1}^{Z}\frac{Ze^2}{\left|r_i-R\right|}\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_Z,\boldsymbol{R}\right)+\sum_{i>j}\frac{e^2}{\left|r_i-r_j\right|}\psi\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_Z,\boldsymbol{R}\right)$$

Note that you can separate the previous equation for the potential of all cars into N different equations:

$$\frac{-\hbar^2}{2m_i}\nabla_i^2\psi_i\left(\boldsymbol{r}_i\right)+V_i\left(\boldsymbol{r}_i\right)\psi_i\left(\boldsymbol{r}_i\right)=E_i\psi_i\left(\boldsymbol{r}_i\right)$$

And the total energy is just the sum of the energies of the individual cars:

$$E=\sum_{i=1}^{N}E_i$$

And the wave function is just the product of the individual wave functions:

$$\psi_{n_1,n_2\ldots,n_N}\left(\boldsymbol{r}_1,\boldsymbol{r}_2,\ldots,\boldsymbol{r}_N\right)=\prod_{i=1}^{N}\psi_{n_i}\left(\boldsymbol{r}_i\right)$$

where the Π symbol is just like Σ, except it stands for a product of terms, not a sum, and n_i refers to all the quantum numbers of the ith particle.

As you can see, when the particles you're working with are distinguishable and subject to independent potentials, the problem of handling many of them becomes simpler. You can break the system up into N independent one-particle systems. The total energy is just the sum of the individual energies of each particle. The Schrödinger equation breaks down into N different equations. And the wave function ends up just being the product of the wave functions of the N different particles.

Take a look at an example. Say you have four particles, each with a different mass, in a square well. You want to find the energy and the wave function of this system. Here's what the potential of the square well looks like this for each of the four noninteracting particles:

$$V_i\left(x_i\right) = \begin{vmatrix} 0 \text{ for } 0 \le x_i \le a \\ \infty \text{ for } x_i > a \\ \infty \text{ for } x_i < 0 \end{vmatrix}$$

Here's what the Schrödinger equation looks like:

$$E\psi_{n_1,n_2,n_3,n_4}\left(x_1,x_2,x_3,x_4\right) = \sum_{i=1}^{4} \frac{-\hbar^2}{2m_i} \frac{d^2}{dx_i^2} \psi_{n_1,n_2,n_3,n_4}\left(x_1,x_2,x_3,x_4\right)$$

You can separate the preceding equation into four one-particle equations:

- $E_1\psi_{n_1}\left(x_1\right) = \frac{-\hbar^2}{2m_1} \frac{d^2}{dx_1^2} \psi_{n_1}\left(x_1\right)$

- $E_2\psi_{n_2}\left(x_2\right) = \frac{-\hbar^2}{2m_2} \frac{d^2}{dx_2^2} \psi_{n_2}\left(x_2\right)$

- $E_3\psi_{n_3}\left(x_3\right) = \frac{-\hbar^2}{2m_3} \frac{d^2}{dx_3^2} \psi_{n_3}\left(x_3\right)$

- $E_4\psi_{n_4}\left(x_4\right) = \frac{-\hbar^2}{2m_4} \frac{d^2}{dx_4^2} \psi_{n_4}\left(x_4\right)$

I've already solved such one-dimensional problems in Chapter 3. The energy levels are

$$E_i = \frac{\hbar^2 \pi^2 n_i^2}{2m_i a^2}$$

And because the total energy is the sum of the individual energies is $E = \sum_{i=1}^{4} E_i$, the energy in general is

$$E = \frac{\hbar^2 \pi^2}{2a^2} \left[\frac{n_1^2}{m_1} + \frac{n_2^2}{m_2} + \frac{n_3^2}{m_3} + \frac{n_4^2}{m_4} \right]$$

So here's the energy of the ground state — where all particles are in their ground states, $n_1 = n_2 = n_3 = n_4 = 1$:

$$E = \frac{\hbar^2 \pi^2}{2a^2} \left[\frac{1}{m_1} + \frac{1}{m_2} + \frac{1}{m_3} + \frac{1}{m_4} \right]$$

For a one-dimensional system with a particle in a square well, the wave function is

$$\psi_i(x) = \frac{2^{1/2}}{a^{1/2}} \sin\left(\frac{n_i \pi}{a} x_i\right)$$

The wave function for the four-particle system is just the product of the individual wave functions, so it looks like this:

$$\psi_{n_1,n_2,n_3,n_4}(x_1,x_2,x_3,x_4) = \frac{4}{a^2} \sin\left(\frac{n_1 \pi}{a} x_1\right) \sin\left(\frac{n_2 \pi}{a} x_2\right) \sin\left(\frac{n_3 \pi}{a} x_3\right) \sin\left(\frac{n_4 \pi}{a} x_4\right)$$

For example, for the ground state, $n_1 = n_2 = n_3 = n_4 = 1$, you have

$$\psi_{1,1,1,1}(x_1,x_2,x_3,x_4) = \frac{4}{a^2} \sin\left(\frac{\pi}{a} x_1\right) \sin\left(\frac{\pi}{a} x_2\right) \sin\left(\frac{\pi}{a} x_3\right) \sin\left(\frac{\pi}{a} x_4\right)$$

So as you can see, systems of N independent, distinguishable particles are often susceptible to solution — all you have to do is to break them up into N independent equations.

Juggling Many Identical Particles

When the particles in a multi-particle system are all indistinguishable, that's when the real adventure begins. When you can't tell the particles apart, how can you tell which one's where? This section explains what happens.

Losing identity

Say you have a bunch of pool balls and you want to look at them classically. You can paint each pool ball differently, and then, even as they hurtle around the pool table, you're able to distinguish them — seven ball in the corner pocket, and that sort of thing. Classically, identical particles retain their individuality. You can still tell them apart.

The same isn't true quantum mechanically, because identical quantum particles really are identical — you can't paint them, as you can pool balls.

For example, look at the scenario in Figure 10-3. There, two electrons are colliding and bouncing apart. Seems like keeping track of the two electrons would be easy.

Figure 10-3:
An electron
colliding
with another
electron.
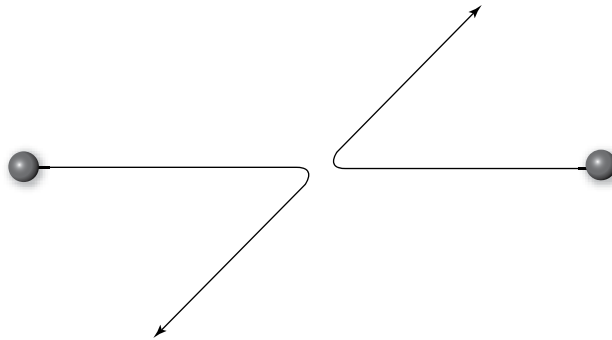
But now look at the scenario in Figure 10-4 — the electrons could've bounced like that, not like the bounce shown in Figure 10-3. And you'd never know it.

Figure 10-4:
An electron
colliding
with another
electron.
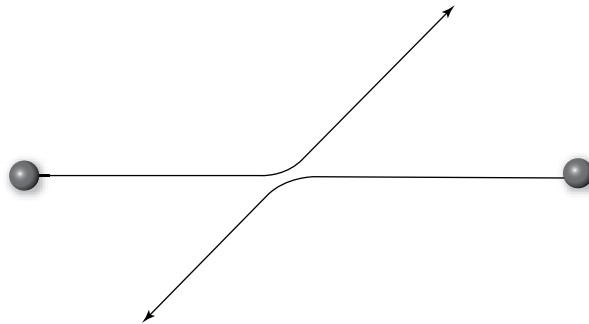
So which electron is which? From the experimenter's point of view, you can't tell. You can place detectors to catch the electrons, but you can't determine which of the incoming electrons ended up in which detector, because of the two possible scenarios in Figures 10-3 and 10-4.

REMEMBER

Quantum mechanically, identical particles don't retain their individuality in terms of any measurable, observable quantity. You lose the individuality of identical particles as soon as you mix them with similar particles. This idea holds true for any N-particle system. As soon as you let N identical particles interact, you can't say which exact one is at r_1 or r_2 or r_3 or r_4 and so on.

Symmetry and antisymmetry

In practical terms, the loss of individuality among identical particles means that the probability density remains unchanged when you exchange particles. For example, if you were to exchange electron 10,281 with electron 59,830, you'd still have the same probability that an electron would occupy $d^3r_{10,281}$ and $d^3r_{59,830}$.

Here's what this idea looks like mathematically (r and s are the location and spins of the particles):

$$|\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_N s_N)|^2 = |\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_N s_N)|^2$$

The preceding equation means that

$$\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_N s_N) = \pm\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_N s_N)$$

REMEMBER

So the wave function of a system of N identical particles must be either symmetric or antisymmetric when you exchange two particles. Spin turns out to be the deciding factor:

- ✔ **Antisymmetric wave function:** If the particles have half-odd-integral spin ($^1/_2$, $^3/_2$, and so on), then this is how the wave function looks under exchange of particles:

$$\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_N s_N) = -\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_N s_N)$$

- ✔ **Symmetric wave function:** If the particles have integral spin (0, 1, and so on), this is how the wave function looks under exchange of particles:

$$\psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_N s_N) = \psi(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_N s_N)$$

Having symmetric or antisymmetric wave functions leads to some different physical behavior, depending on whether the wave function is symmetric or antisymmetric.

REMEMBER

In particular, particles with integral spin, such as photons or pi mesons, are called *bosons*. And particles with half-odd-integral spin, such as electrons, protons, and neutrons, are called *fermions*. The behavior of systems of fermions is very different from the behavior of systems of bosons.

Exchange degeneracy: The steady Hamiltonian

The Hamiltonian, which you can represent like this

$$\mathrm{H}(\mathbf{r}_1 s_1, \mathbf{r}_2 s_2, ..., \mathbf{r}_i s_i, ..., \mathbf{r}_j s_j, ..., \mathbf{r}_N s_N)$$

doesn't vary under exchange of two identical particles. In other words, the Hamiltonian is invariant here, no matter how many identical particles you exchange. That's called *exchange degeneracy,* and mathematically, it looks like this:

$$H(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, ..., \boldsymbol{r}_i s_i, ..., \boldsymbol{r}_j s_j, ..., \boldsymbol{r}_N s_N) = H(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, ..., \boldsymbol{r}_j s_j, ..., \boldsymbol{r}_i s_i, ..., \boldsymbol{r}_N s_N)$$

That means, incidentally, that the exchange operator, P_{ij}, is an invariant of the motion because it commutes with the Hamiltonian:

$$[H, P_{ij}] = 0$$

Name that composite: Grooving with the symmetrization postulate

In the earlier section titled "Symmetry and antisymmetry," I show that the wave function of a system of N particles is either symmetric or antisymmetric under the exchange of two particles:

- **Symmetric:** $\psi(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, ..., \boldsymbol{r}_i s_i, ..., \boldsymbol{r}_j s_j, ..., \boldsymbol{r}_N s_N) = \psi(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, ..., \boldsymbol{r}_j s_j, ..., \boldsymbol{r}_i s_i, ..., \boldsymbol{r}_N s_N)$

- **Antisymmetric:** $\psi(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, ..., \boldsymbol{r}_i s_i, ..., \boldsymbol{r}_j s_j, ..., \boldsymbol{r}_N s_N) = -\psi(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, ..., \boldsymbol{r}_j s_j, ..., \boldsymbol{r}_i s_i, ..., \boldsymbol{r}_N s_N)$

This turns out to be the basis of the *symmetrization postulate,* which says that in systems of N identical particles, only states that are symmetric or antisymmetric exist — and it says that states of mixed symmetry don't exist.

The symmetrization postulate also says, as observed from nature, that

- Particles with half-odd-integral states ($^1/_2$, $^3/_2$, $^5/_2$, ...) are *fermions,* and they have antisymmetric states under the interchange of two particles.

- Particles with integral spin (0, 1, 2, ...) are *bosons,* and they have symmetric states under the interchange of two particles.

So the wave function of N fermions is completely antisymmetric, and the wave function of N bosons is completely symmetric.

Determining whether a particle is a fermion or a boson may seem like an easy task — just look it up. Electrons, protons, and neutrons are fermions, for example, with half-odd-integral spin. And photons, pi mesons, and so on are bosons, with integral spins.

But what if the particle you're studying is a composite particle? What if, for example, you have an *alpha particle,* which is made up of two protons and two neutrons? Is that a fermion or a boson?

In fact, protons and neutrons themselves are made up of three quarks, and pi mesons are made up of two — and quarks have spin $1/2$.

Composites can be either fermions or bosons — it all depends on whether the spin of the composite particle ends up being half-odd-integral or integral. If the composite particle's spin is $1/2$, $3/2$, $5/2$, and so on, then the composite particle is a fermion. If the composite particle's spin is 0, 1, 2, and so on, then the composite particle is a boson.

TIP

In general, if the composite particle is made up of an odd number of fermions, then it's a fermion. Otherwise, it's a boson. So for example, because quarks are fermions and because nucleons such as protons and neutrons are made up of three quarks, those nucleons end up being fermions. But because pi mesons are made up of two quarks, they end up being bosons. The alpha particle, which consists of two protons and two neutrons, is a boson. You can even consider whole atoms to be composite particles. For example, consider the hydrogen atom: That atom is made up of a proton (a fermion) and an electron (another fermion), so that's two fermions. And that makes the hydrogen atom a boson.

Building Symmetric and Antisymmetric Wave Functions

Many of the wave functions that are solutions to physical setups like the square well aren't inherently symmetric or antisymmetric; they're simply *asymmetric.* In other words, they have no definite symmetry. So how do you end up with symmetric or antisymmetric wave functions?

The answer is that you have to create them yourself, and you do that by adding together asymmetric wave functions. For example, say that you have an asymmetric wave function of two particles, $\psi(r_1s_1, r_2s_2)$.

TIP

To create a symmetric wave function, add together $\psi(r_1s_1, r_2s_2)$ and the version where the two particles are swapped, $\psi(r_2s_2, r_1s_1)$. Assuming that $\psi(r_1s_1, r_2s_2)$ and $\psi(r_2s_2, r_1s_1)$ are normalized, you can create a symmetric wave function using these two wave functions this way — just by adding the wave functions:

$$\psi_s\left(r_1s_1, r_2s_2\right) = \frac{1}{\sqrt{2}}\left[\psi\left(r_1s_1, r_2s_2\right) + \psi\left(r_2s_2, r_1s_1\right)\right]$$

You can make an antisymmetric wave function by subtracting the two wave functions:

$$\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) = \frac{1}{\sqrt{2}}\left[\psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) - \left(\boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1\right)\right]$$

This process gets rapidly more complex the more particles you add, however, because you have to interchange all the particles. For example, what would a symmetric wave function based on the asymmetric three-particle wave function $\psi(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3)$ look like? Why, it'd look like this:

$$\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3\right) = \frac{1}{\sqrt{6}}\Big[\psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3\right) + \psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_3 s_3, \boldsymbol{r}_2 s_2\right)$$
$$+ \psi\left(\boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3, \boldsymbol{r}_1 s_1\right) + \psi\left(\boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1, \boldsymbol{r}_3 s_3\right)$$
$$+ \psi\left(\boldsymbol{r}_3 s_3, \boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) + \psi\left(\boldsymbol{r}_3 s_3, \boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1\right)\Big]$$

And how about the antisymmetric wave function? That looks like this:

$$\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3\right) =$$
$$\frac{1}{\sqrt{6}}\begin{bmatrix}\psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3\right) - \psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_3 s_3, \boldsymbol{r}_2 s_2\right) + \psi\left(\boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3, \boldsymbol{r}_1 s_1\right) \\ -\psi(\boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1, \boldsymbol{r}_3 s_3) + \psi\left(\boldsymbol{r}_3 s_3, \boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) - \psi\left(\boldsymbol{r}_3 s_3, \boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1\right)\end{bmatrix}$$

And in this way, at least theoretically, you can create symmetric and antisymmetric wave functions for any system of N particles.

Working with Identical Noninteracting Particles

Working with identical noninteracting particles makes life easier because you can treat the equations individually instead of combining them into one big mess. Say you have a system of N identical particles, each of which experiences the same potential. You can separate the Schrödinger equation into N identical single-particle equations:

$$\frac{-\hbar^2}{2m_i}\nabla_i^{\,2}\psi_i\left(\boldsymbol{r}_i\right) + V_i\left(\boldsymbol{r}_i\right)\psi_i\left(\boldsymbol{r}_i\right) = E_i\psi_i\left(\boldsymbol{r}_i\right)$$

And the total energy is just the sum of the energies of the individual particles:

$$E = \sum_{i=1}^{N} E_i$$

But now look at the wave function for the system. Earlier in the chapter (see "Floating Cars: Tackling Systems of Many Distinguishable Particles"), you consider the wave function of a system of N distinguishable particles and come up with the product of all the individual wave functions:

$$\psi_{n_1, n_2, \ldots, n_N}\left(\boldsymbol{r}_1, \boldsymbol{r}_2, \ldots, \boldsymbol{r}_N\right) = \prod_{i=1}^{N} \psi_{n_i}\left(\boldsymbol{r}_i\right)$$

However, that equation doesn't work with identical particles because you can't say that particle 1 is in state $\psi_1(\boldsymbol{r}_1)$, particle 2 is in state $\psi_2(\boldsymbol{r}_2)$, and so on — they're identical particles here, not distinguishable particles as before.

The other reason this equation doesn't work here is that it has no inherent symmetry — and systems of N identical particles must have a definite symmetry. So instead of simply multiplying the wave functions, you have to be a little more careful.

Wave functions of two-particle systems

How do you create symmetric and antisymmetric wave functions for a two-particle system? Start with the single-particle wave functions (see the earlier section "Building Symmetric and Antisymmetric Wave Functions"):

➤ $\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) = \dfrac{1}{\sqrt{2}}\left[\psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) + \psi\left(\boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1\right)\right]$

➤ $\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) = \dfrac{1}{\sqrt{2}}\left[\psi\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) - \left(\boldsymbol{r}_2 s_2, \boldsymbol{r}_1 s_1\right)\right]$

By analogy, here's the symmetric wave function, this time made up of two single-particle wave functions:

$$\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right) = \dfrac{1}{\sqrt{2}}\left[\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right) + \psi_{n_1}\left(\boldsymbol{r}_2 s_2\right)\psi_{n_2}\left(\boldsymbol{r}_1 s_1\right)\right]$$

And here's the antisymmetric wave function, made up of the two single-particle wave functions:

$$\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right)=\frac{1}{\sqrt{2}}\Big[\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)-\psi_{n_1}\left(\boldsymbol{r}_2 s_2\right)\psi_{n_2}\left(\boldsymbol{r}_1 s_1\right)\Big]$$

where n_i stands for all the quantum numbers of the ith particle.

Note in particular that $\psi_a(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2)$ = 0 when $n_1 = n_2$; in other words, the antisymmetric wave function vanishes when the two particles have the same set of quantum numbers — that is, when they're in the same quantum state. That idea has important physical ramifications.

You can also write $\psi_s(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2)$ like this, where P is the permutation operator, which takes the permutation of its argument:

$$\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right)=\frac{1}{\sqrt{2!}}\sum_{\text{P}}\text{P}\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)$$

And also note that you can write $\psi_a(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2)$ like this:

$$\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right)=\frac{1}{\sqrt{2!}}\sum_{\text{P}}(-1)^{\text{P}}\text{P}\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)$$

where the term $(-1)^{\text{P}}$ is 1 for even permutations (where you exchange both $\boldsymbol{r}_1 s_1$ and $\boldsymbol{r}_2 s_2$ and also n_1 and n_2) and –1 for odd permutations (where you exchange $\boldsymbol{r}_1 s_1$ and $\boldsymbol{r}_2 s_2$ but not n_1 and n_2; or you exchange n_1 and n_2 but not $\boldsymbol{r}_1 s_1$ and $\boldsymbol{r}_2 s_2$).

In fact, people sometimes write $\psi_a(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2)$ in determinant form like this:

$$\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2\right)=\frac{1}{\sqrt{2!}}\det\begin{vmatrix}\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right) & \psi_{n_1}\left(\boldsymbol{r}_2 s_2\right)\\ \psi_{n_2}\left(\boldsymbol{r}_1 s_1\right) & \psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)\end{vmatrix}$$

Note that this determinant is zero if $n_1 = n_2$.

Wave functions of three-or-more-particle systems

Now you get to put together the wave function of a system of three particles from single-particle wave functions.

The symmetric wave function looks like this:

$$\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3\right) = \frac{1}{\sqrt{3!}}\sum_P P\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)\psi_{n_3}\left(\boldsymbol{r}_3 s_3\right)$$

And the antisymmetric wave function looks like this:

$$\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \boldsymbol{r}_3 s_3\right) = \frac{1}{\sqrt{3!}}\sum_P (-1)^P \psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)\psi_{n_3}\left(\boldsymbol{r}_3 s_3\right)$$

This asymmetric wave function goes to zero if any two single particles have the same set of quantum numbers ($n_i = n_j, \ i \neq j$).

How about generalizing this to systems of N particles? If you have a system of N particles, the symmetric wave function looks like this:

$$\psi_s\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \ldots, \boldsymbol{r}_N s_N\right) = \frac{1}{\sqrt{N!}}\sum_P P\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)\ldots\psi_{n_N}\left(\boldsymbol{r}_N s_N\right)$$

And the antisymmetric wave function looks like this:

$$\psi_a\left(\boldsymbol{r}_1 s_1, \boldsymbol{r}_2 s_2, \ldots, \boldsymbol{r}_N s_N\right) = \frac{1}{\sqrt{N!}}\sum_P (-1)^P P\psi_{n_1}\left(\boldsymbol{r}_1 s_1\right)\psi_{n_2}\left(\boldsymbol{r}_2 s_2\right)\ldots\psi_{n_N}\left(\boldsymbol{r}_N s_N\right)$$

The big news is that the antisymmetric wave function for N particles goes to zero if any two particles have the same quantum numbers ($n_i = n_j, \ i \neq j$). And that has a big effect in physics, as you see next.

It's Not Come One, Come All: The Pauli Exclusion Principle

The antisymmetric wave function vanishes if any two particles in an N-particle system have the same quantum numbers. Because fermions are the type of particles that have antisymmetric wave functions, that's the equivalent of saying that in a system of N particles, no two fermions can have the same quantum numbers — that is, occupy the same state.

That idea, which Austrian physicist Wolfgang Pauli first formulated in 1925, is called the *Pauli exclusion principle*. The topic of discussion at that time was the atom, and the Pauli exclusion principle applied to the electrons (a type of fermion), which are present in all atoms.

The *Pauli exclusion principle* states that no two electrons can occupy the same quantum state inside a single atom. And that result is important for the structure of atoms. Instead of just piling on willy-nilly, electrons have to fill quantum states that aren't already taken. The same isn't true for bosons — for example, if you have a heap of alpha particles (bosons), they can all be in the same quantum state. Not so for fermions.

There are various quantum numbers that electrons can take in an atom — n (the energy), l (the angular momentum), m (the z component of the angular momentum), and m_s (the z component of spin). And using that information, you can construct the electron structure of atoms.

Figuring out the Periodic Table

One of the biggest successes of the Schrödinger equation, together with the Pauli exclusion principle (see the preceding section), is explaining the electron structure of atoms.

The electrons in an atom have a shell structure, and they fill that structure based on the Pauli exclusion principle, which maintains that no two electrons can have the same state:

✔ The major shells are specified by the principal quantum number, n, corresponding to the distance of the electron from the nucleus.

✔ Shells, in turn, have subshells based on the orbital angular momentum quantum number, l.

✔ In turn, each subshell has subshells — called *orbitals* — which are based on the z component of the angular momentum, m.

So each shell n has $n - 1$ subshells, corresponding to $l = 0, 1, 2, ..., n - 1$. And in turn, each subshell has $2l + 1$ orbitals, corresponding to $m = -1, -l + 1, ..., l - 1, l$.

Much as with the hydrogen atom, the various subshells ($l = 0, 1, 2, 3, 4$, and so on) are called the *s, p, d, f, g, h*, and so on states. So, for example, for a given n, an s state has one orbital ($m = 0$), a p state has three orbitals ($m = -1$, 0, and 1), a d state has five orbitals ($m = -2, -1, 0, 1$, and 2), and so on.

In addition, due to the z component of the spin, m_s, each orbital can contain two electrons — one with spin up, and one with spin down.

So how do the electrons, as fermions, fill the structure of an atom? Electrons can't fill a quantum state that's already been taken. For atoms in the ground state, electrons fill the orbitals in order of increasing energy. As soon as all of a subshell's orbitals are filled, the next electron goes on to the next sub-shell; and when the subshell is filled, the next electron goes on to the next shell, and so on.

Of course, as you fill the different electron shells, subshells, and orbitals, you end up with a different electron structure. And because interactions between electrons form the basis of chemistry, as electrons fill the successive quantum levels in various atoms, you end up with different chemical properties for those atoms — which set up the period (row) and group (column) organization of the periodic table.