Physical Quantities: Eigenvalues and Eigenvectors
Physics 223

The plan:
This week we'll connect the mathematical formalism to the physics. The connection is provided through the postulates (*i.e.*, underivable) of quantum mechanics. After we list and discuss the postulates, we'll investigate some mathematical (and physical) consequences.

The Postulates:
1) The behavior of quantum mechanical entities (that is, everything) is completely determined by a "wave function," which we usually write $\psi(x,t)$. Everything is determined by ψ. There is no other information to be had.

The fact that the wave function contains all the information will lead to the uncomfortable conclusion that we can't know as much about the world as we used to think we could, in "classical" (Newtonian) physics. This loss of information led Einstein to reject QM as an incomplete theory. Unterstanding that rejection is the ultimate goal of this course.

2) The behavior of $\psi(x,t)$ is governed by Schrödinger's equation:

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

Each term in this equation has a specific physical meaning that we'll discuss below. Note that because of the *i* in the equation, solutions will, in general, be complex functions.

There's a lot of talk in QM about the loss of determinism, that one can't predict the future. It's important to keep in mind that the wave function itself evolves deterministically, as per Schrödinger's equation.

Note: The equation we've written only describes one object. Schrödinger's equation for many objects rapidly becomes very complicated. We'll discuss later in this course a simpler way to describe multiparticle systems.

3) $\psi(x,t)$ tells us the probability density to find the object (if you look for it) near position x at time t. The probability is given by, $P(x,t) = |\psi(x,t)|^2 \equiv \psi^*(x,t)\psi(x,t)$. Note that, because total probability is always 1, the norm of ψ (the integral over all space of $|\psi|^2$) is always 1.

Why to I add the phrase "if you look for it"? This is a reminder that in quantum mechanics, one cannot give a definite answer to answer the question, "Where was the electron *before* we measured its position?" The correct response is, "The electron that is described by $\psi(x,t)$ does not have any specific position. It has only probabilities." We'll investigate this point more later.

4) Measurements of physical quantities (*e.g.*, energy and momentum) depend on the behavior of operators associated with these quantities. Some of the important behaviors are listed here:

a) For each operator, **O**, (for example, $\partial/\partial x$) there are functions, f, for which $\mathbf{O}f = af$. These are called "eigenfunctions" of **O**, and the numbers, a, are called **O**'s "eigenvalues."

b) When you measure a physical quantity, the result is always one of the eigenvalues of the corresponding operator (assuming you haven't made a sloppy measurement). The probability of obtaining a particular eigenvalue is the square of the projection of ψ onto the corresponding eigenvector.

c) After the measurement, ψ becomes the eigenfunction that corresponds to the eigenvalue you just obtained.

The last point is often referred to as "the collapse of the wave function," because the time dependence of the wave function is discontinuous when a measurement is made. I don't know if we'll have time to discuss this further. The issue of what constitutes a measurement is one of the big unsolved problems in QM. If you're interested, take Physics 419, "Space, Time, and Matter."

The nomenclature comes from the German *eigen* meaning "inherent, or characteristic."

Notation: It is very common to write the operator associated with quantity q, as the same symbol with a "hat," $\hat{q}$. So, the momentum operator is written as $\hat{p}$.

The connection between measurements and operators, and the special role played by the eigenvalues and eigenvectors, is what makes the matrix formulation so useful.

Eigenvalues and eigenvectors:

Solving problems in quantum mechanics often involves finding eigenvalues and eigenvectors. This is a nice problem in matrix algebra. Suppose we have a symmetric 3×3 matrix, **M**. For example:

$$\mathbf{M} = \begin{pmatrix} 2 & 3 & 5 \\ 3 & -1 & 4 \\ 5 & 4 & 4 \end{pmatrix}. \text{ In general, write } \mathbf{M} = \begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{21} & m_{22} & m_{23} \\ m_{31} & m_{32} & m_{33} \end{pmatrix}, \text{ where } m_{ij} = m_{ji}.$$

We'd like to find its eigenvalues and eigenvectors.

I've chosen a symmetric matrix, because the matrix description of all physical operators is symmetric.

Finding the eigenvalues and eigenvectors reduces to solving three simultaneous equations in three unknowns:

$$\mathbf{MV} = \begin{pmatrix} m_{11} & m_{12} & m_{13} \\ m_{21} & m_{22} & m_{23} \\ m_{31} & m_{32} & m_{33} \end{pmatrix} \begin{pmatrix} V_1 \\ V_2 \\ V_3 \end{pmatrix} = \lambda \mathbf{V},$$

where V_1, V_2, and V_3 the components of the eigenvector, are the unknowns. Actually, there are *four* unknowns, because we don't know λ (the eigenvalue) either. However, λ is determined by by observing that a simultaneous set of homogeneous equations has a nontrivial (*i.e.*, nonzero) solution only if the determinant of the coefficients is zero:

$$\begin{vmatrix} m_{11}-\lambda & m_{12} & m_{13} \\ m_{21} & m_{22}-\lambda & m_{23} \\ m_{31} & m_{32} & m_{33}-\lambda \end{vmatrix} = 0$$

This is a third order polynomial equation for λ, so it has three roots, the three eigenvalues of **M**. For each λ, there is an eigenvector **V**.

One property of symmetric matrices is that its eigenvectors are orthogonal. That means that we can use them as an orthornormal basis of the vector space. The physical implication is important: **The eigenvectors of each physical quantity form an orthornormal basis.** That means that every wave function can be written as a linear combination (superposition) of the eigenvectors:

$$\psi = \sum_i c_i \mathbf{V}_i \, .$$

V*i* here means the i^{th} eigenvector, not the i^{th} component of a particular vector. Remember, ψ is an element of the vector space of solutions to Schrödinger's equation, so it is a linear combination of the basis vectors.

Making a measurement:

Suppose our quantum object is described by the wave function $\psi = \sum c_i \mathbf{V}_i$, and we make a measurement of the quantity described by **M**. What result will we obtain? We know from postulate 4b) that we'll obtain one of the eigenvalues, λ_i. But what are the probabilities?

The total probability is one, so $|\psi|^2 = 1$. We say, "ψ is normalized." Let's write ψ in terms of the basis vectors:

$$|\psi|^2 = \left|\sum c_i \mathbf{V}_i\right|^2 = \sum c_i^2 = 1.$$

The last equality holds because the **V**'s are an orthonormal basis. This isn't a surprising result; you saw this manipulation before. I wrote it again to suggest the answer to the probability question:

> Suppose you measure a physical quantity q. The probability of obtaining q_i, the i^{th} eigenvalue, is c_i^2, the square of the component of the wave function along $\mathbf{V}_i$, the i^{th} eigenvector.

If the numbers and functions are complex, replace c^2 with c^*c. (c^* is the complex conjugate.)

An example, momentum:

You will learn in Physics 214 that the momentum of a quantum object is related to the wavelength of the wave function. $p = h/\lambda = \hbar k$, where h is Planck's constant and $\hbar = h/2\pi$. What linear operator will tell give us this result?

We want to find an operator that has eigenvalues equal to $\hbar k$ (k alone will do; we can multiply by $\hbar$ at the end). Applying the x derivative to sin(kx) and cos(kx) almost works but fails because sin $\leftrightarrow$ cos. However, the exponential works fine:

$$\frac{d}{dx}e^{ikx} = ike^{ikx} \quad \Rightarrow \quad -i\hbar\frac{d}{dx}e^{ikx} = (\hbar k)e^{ikx}$$

So, the operator that corresponds to momentum is $-i\hbar d/dx$. We need the i in the exponent (and, as a consequence, in the operator) to make it a wave, not just a rising or falling function.

What does this mean?

- The wave function, $\psi(x)$ that describes an object with a specific value, p, of momentum is e^{ikx}, where $k = p/\hbar$. This function is an eigenvector of the momentum operator with eigenvalue p. In QM, one often uses the word "eigenstate," because it's the "state" of the object.

- Suppose $\psi(x) = e^{ikx}$. What is the probability density as a function of x? ψ is complex, so we must use $\psi^*\psi$, not ψ^2. Thus, $P(x) = \psi^*(x)\psi(x) = 1$, so the probability density is the same everywhere! What does this mean?

  The e^{ikx} function spreads out from $-\infty < x < \infty$. This tells us that any object confined to a finite spatial region cannot be in a state of definite momentum. Does this make sense? Here's my logic: In order for momentum to have a definite value, there must not be any forces acting (otherwise momentum is changing). Thus the potential energy is constant, and there are no "holes" for the object to fall into. It can be anywhere.

  The probability density cannot = 1 everywhere, because then the total probability would be infinite. We need to normalize ψ ($\psi \rightarrow N\psi$). Unfortuantely, because of the infinite spatial extent, $N = 0$. This problem requires a bit of trickery to deal with, so I'm going to ignore it for now. (No real object is spread out to infinity in any case.)

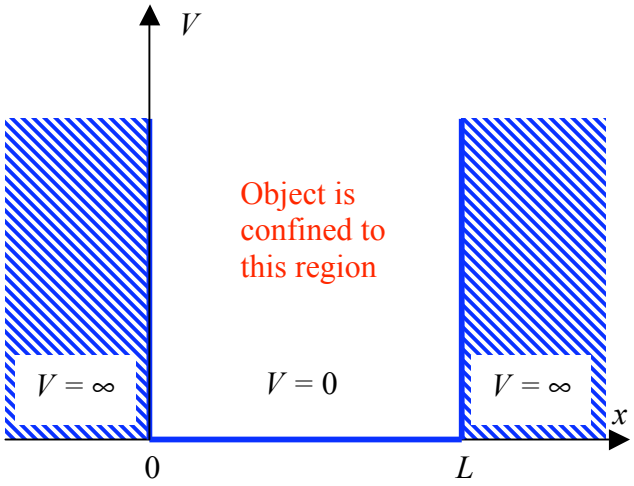
I'll discuss the momentum operator more in a while. First, I want to bring in Schödinger's equation and solve a problem, the particle in a box. You'll do this problem in detail in week 4 of Physics 214. After we solve this problem, it will be easier to gain some intuition about the behavior of quantum objects.

Particle in a Box:

Imagine a particle moving freely within a finite 1-dimensional region, $0 \le x \le L$. In this region, the potential energy is constant (no force), so set $V = 0$. The walls are very hard (impenetrable). We describe this by setting $V = \infty$ for $x < 0$ and $x > L$.

Classically (according to Newton), the particle will bounce back and forth. If its total energy is E, then its momentum will be $+\sqrt{(2mE)}$ half of the time and $-\sqrt{(2mE)}$ the other half. The average momentum is zero.

We learn about the quantum behavior by solving Schrödinger's equation. Because the potential energy is not described by a single function, we must solve separately for ψ inside and outside the box.



Inside the box:

With $V = 0$, S's equation becomes $-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} = i\hbar\frac{\partial\psi}{\partial t}$. This equation is most easily solved by looking for a wave function that is an eigenvector of both operators, $\partial/\partial t$ and $\partial^2/\partial x^2$. That's a standard trick in differential equations. It's called "separating" the functions. (Caveat: Not every diff. eq. allows this.)

- The time derivative.
  This is exactly the same as the momentum operator (except that it's t, not x), so the solutions are also exponentials:

$$\Psi(x,t) = f(x)e^{-i\omega t}. \quad \frac{\partial\Psi(x,t)}{\partial x} = -i\omega f(x)e^{-i\omega t} = -i\omega\Psi$$

  Any f will do. We now have $i\hbar\frac{\partial\Psi}{\partial t} = \hbar\omega\Psi = E\Psi$. Thus,

  $i\hbar\partial/\partial t$ is the operator associated with total energy!

  Just as objects with a particular momentum have a definite wavelength, objects with a particular energy have a definite frequency. This behavior allows us to simplify the problem. Whenever we are considering objects that have a definite energy, we only need to deal with the "time independent Schrödinger's equation":

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V\psi(x) = E\psi(x).$$

Note that $\psi(x)$ has only spatial dependence. The complete wave function is: $\Psi(x,t) = \psi(x)e^{-i\omega t}$. As in Physics 214, I'll use capital and lower case to distinguish the two functions.

- <u>The space derivative.</u>

  Recall that the momentum operator is $\hat{p} = -i\hbar\frac{\partial}{\partial x}$. What happens if we apply $\hat{p}$ to ψ twice? If ψ is a momentum eigenstate ($\hat{p}\psi = p\psi$), then $\hat{p}\hat{p}\psi = \hat{p}(\hat{p}\psi) = p^2\psi$. So, $\hat{p}\hat{p}$ is the p^2 operator. But notice what this is in terms of derivatives:

$$\left(-i\hbar\frac{\partial}{\partial x}\right)\left(-i\hbar\frac{\partial}{\partial x}\right) = -\hbar^2\frac{\partial^2}{\partial x^2}.$$

  The left side of Schrödinger's equation is just the kinetic energy, $p^2/2m$. Schrödinger's equation is the quantum mechanical expression of the relation petween momentum and energy, $p^2/2m = E$. In problems where $V \neq 0$, the equation is telling us that $p^2/2m + V = E$.

$-\hbar^2\partial^2/\partial x^2$ is the operator associated with kinetic energy.

  What are the eigenvectors of $\hat{p}^2$? e^{ikx} works just as it did for $\hat{p}$, but now $\sin(kx)$ and $\cos(kx)$ also work. That is, it is possible for a wave function to have a definite kinetic energy even though it doesn't have a definite momentum.

- <u>Which eigenvectors to use?</u>

  You'll discuss the particle in a box in Physics 214, so I won't go through it here. If you want to see a detailed treatment, look at the appendix to this note. It turns out that we want the $\sin(kx)$ solutions, because they go to zero at $x = 0$ and $x = L$. To make $\sin(kx)$ go to zero at $x = L$, k can only have certain values: $k_n = n\pi/L$, for any positive integer n.

  So, the complete solution is, $\Psi_n(x,t) = A\sin(k_n x)e^{-i\omega_n t}\,t$. In order to satisfy Schrödinger's equation, k and ω are related: $\hbar\omega = (\hbar k)^2/2m$. This is just $E = p^2/2m$.

Measurement of energy and momentum:

It's interesting to think about the momentum of the particle. If we measure the momentum, we'll get an eigenvalue of the momentum operator, and the wave function will become the corresponding eigenstate. Sin(kx) is not one of these eigenstates; it's a superposition:

$$\sin(kx) = (e^{ikx} - e^{-ikx})/2i$$

This means that if the particle has a definite energy you cannot predict with certainty the result of a momentum measurement. Also, after the momentum measurement it will no longer have a definite energy.

There is an important conceptual issue. Looking at the equation above, you can see that you'll sometimes measure a positive momentum and sometimes a negative momentum. This seems to be the same as in the classical situation, where the ball is moving to the left half of the time and to the right half of the time, as it bounces off the walls. Is this what's happening in QM?

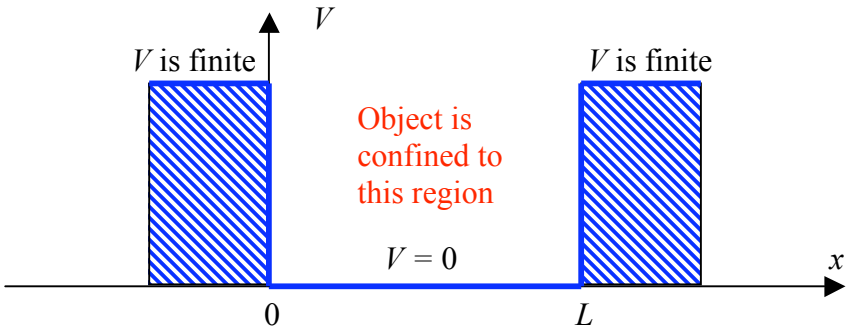
The quantum situation is not the same as the classical one!!!

It is not correct to think that the particle has some value of the momentum, but that we happen not to know what it is. We'll see later in the course that this idea (called "realism") leads to incorrect predictions. In the situation at hand, the particle really has no definite value of the momentum. In some sense, our measurement gives it one.

Appendix:

Boundary conditions on ψ and the solution of the finite and infinite square well. You'll do this problem in P214. I include it here for completeness, but you can skip it.

To solve the square well problem, we need to look at the forbidden regions ($x < 0$ and $x > L$). Having an infinite potential makes this difficult, so let's back off to a simpler situation:



Now that V is finite, Schrödinger's equation is much better behaved. Schrödonger's equation in the forbidden regions is (collecting constants on the right):

$$\frac{d^2\psi(x)}{dx^2} = \frac{2m(V-E)}{\hbar^2}\psi(x)$$, where V-E is a **positive** constant, if the particle is trapped.

The solution is an exponential with a real (not imaginary) exponent, $\psi(x) = e^{\pm\kappa x\, x}$. The constant $\kappa = \sqrt{[2m(V\text{-}E)]}/\hbar$. To keep $\psi(x)$ well behaved (not tending to infinity) we must choose the positive exponent on the left ($x < 0$) and the negative exponent on the right ($x > L$).

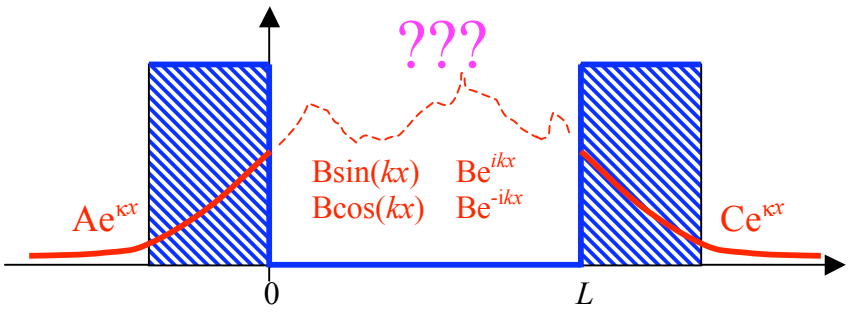
Comment:

> The behavior in the forbidden region illustrates an important difference between classical and quantum behavior. In classical physics, the particle is not allowed in any region where $V > E$. In QM, the particle is allowed to penetrate into a classically forbidden region, as long as V is finite. Many useful applications (*e.g.*, scanning tunneling microscopes) take advantage of this behavior.

Look at what Schrödinger's equation tells us about the continuity of ψ. Wherever V is finite, the second derivative must be finite, which imposes two boundary conditions on ψ:

Both ψ and $d\psi/dx$ must be continuous wherever V is finite.

Now, the situation is:



We'll use the boundary conditions to give us relations between the normalization constants. k and κ are both known constants (they depend on E): $k = \sqrt{[2mE]}/\hbar$, and $\kappa = \sqrt{[2m(V-E)]}/\hbar$.

At x = 0:	Continuity of ψ:	Continuity of $d\psi/dx$:
• Try $B\cos(kx)$: $A = B = 0$. No solution	$A = B$	$A\kappa = 0$
• Try $B\sin(kx)$: $A = B = 0$ again.	$A = 0$	$A\kappa = kB$
• Try $Be^{\pm ikx}$: These equations are only consistent if $\kappa = \pm ik$. This only holds when $V = 0$. Not a general solution.	$A = B$	$A\kappa = \pm ikB$
• Try $B\sin(kx) + D\cos(kx)$: The solution requires that $D = (k/\kappa)B$. That's OK.	$A = D$	$A\kappa = kB$
• Try $Be^{+ikx} + De^{-ikx}$: This requires $B(1-ik/\kappa) = D(1+ik/\kappa)$. I won't prove it, but this solution is the same as the one above.	$A = B+D$	$A\kappa = ik(B-D)$

We can simplify the solution. $B(\sin(kx) + (k/\kappa)\cos(kx)) = (B\sec\delta)\sin(kx+\delta)$, where I've defined $\tan\delta \equiv k/\kappa$. (This is just manipulation of trig identities.) So the general solution in the allowed region is a sine function with a "phase shift," δ, that depends on E.

At $x = L$: $B\sec\delta\sin(kL+\delta) = Ce^{-\kappa L}$ $kB\sec\delta\cos(kL+\delta) = -\kappa Ce^{-\kappa L}$

We have two equations in one unknown, C. Eliminating C from the equations yields a relation that must be satisfied in order to have a solution:

$$-k/\kappa = \tan(kL+\delta)$$

This is a transcendental equation for the energy that can only be solved numerically. We'll see in a minute that this equation is telling us that:

Only certain particle energies are allowed in the well.

To see this, let's look at the infinite well problem. Then, the transcendental equation becomes tractable. When $V \to \infty$, then $V\text{-}E \to \infty$, and so does κ. Therefore:

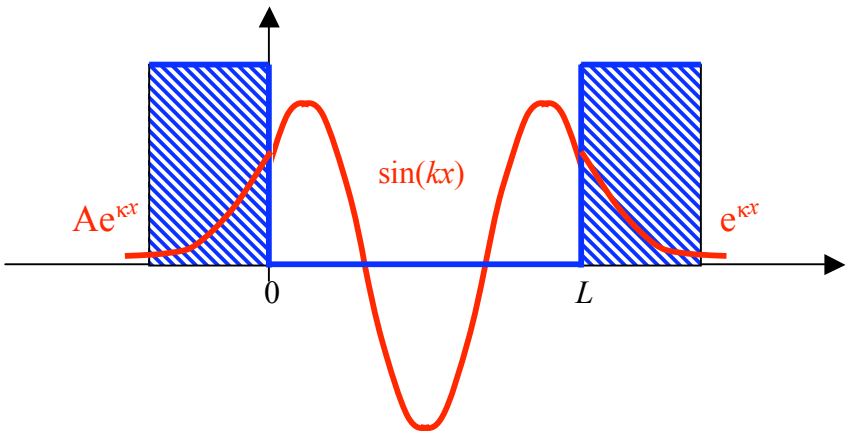
- The exponentials in the forbidden region both become zero ($e^{-\infty} = 0$). Therefore, continuity requires that $\psi(x) = 0$ at both walls ($x = 0$ and $x = L$).
- $\kappa = \infty$ means that $\tan\delta = 0$. Thus $\delta = 0$. Therefore, the transcendental equation above simplifies to $\tan(kL) = 0$. The solutions to this equation are: $kL = n\pi$, where n is any integer.

In an infinitely deep square potential well of width L, the solutions are the same as waves on a string of length L with the ends held fixed. In the quantum situation, discrete wavelengths imply discrete energy values ("levels"):

$$E_n = (\hbar k)^2/2m = (n\pi\hbar)^2/2L^2$$

The solutions look like this:

Finite well: (This is $n = 3$)



Infinite well: (This is $n = 3$)

Note that as $V \to \infty$, ψ remains continuous at the walls, but $d\psi/dx$ develops a kink. That's a result of $\kappa \to \infty$.