

## Operators

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### 20-1 Operations and operators

All the things we have done so far in quantum mechanics could be handled with ordinary algebra, although we did from time to time show you some special ways of writing quantum-mechanical quantities and equations. We would like now to talk some more about some interesting and useful mathematical ways of describing quantum-mechanical things. There are many ways of approaching the subject of quantum mechanics, and most books use a different approach from the one we have taken. As you go on to read other books you might not see right away the connections of what you will find in them to what we have been doing. Although we will also be able to get a few useful results, the main purpose of this chapter is to tell you about some of the different ways of writing the same physics. Knowing them you should be able to understand better what other people are saying. When people were first working out classical mechanics they always wrote all the equations in terms of  $x$ -,  $y$ -, and  $z$ -components. Then someone came along and pointed out that all of the writing could be made much simpler by inventing the vector notation. It's true that when you come down to figuring something out you often have to convert the vectors back to their components. But it's generally much easier to see what's going on when you work with vectors and also easier to do many of the calculations. In quantum mechanics we were able to write many things in a simpler way by using the idea of the "state vector." The state vector  $|\psi\rangle$  has, of course, nothing to do with geometric vectors in three dimensions but is an abstract symbol that *stands for a physical state*, identified by the "label," or "name,"  $\psi$ . The idea is useful because the laws of quantum mechanics can be written as algebraic equations in terms of these symbols. For instance, our fundamental law that any state can be made up from a linear combination of base states is written as

$$|\psi\rangle = \sum_i C_i |i\rangle, \quad (20.1)$$

where the  $C_i$  are a set of ordinary (complex) numbers—the amplitudes  $C_i = \langle i | \psi \rangle$ —while  $|1\rangle$ ,  $|2\rangle$ ,  $|3\rangle$ , and so on, stand for the base states in some base, or *representation*.

If you take some physical state and do something to it—like rotating it, or like waiting for the time  $\Delta t$ —you get a different state. We say, "performing an operation on a state produces a new state." We can express the same idea by an equation:

$$|\phi\rangle = \hat{A} |\psi\rangle. \quad (20.2)$$

An operation on a state produces another state. The *operator*  $\hat{A}$  stands for some particular operation. When this operation is performed on any state, say  $|\psi\rangle$ , it produces some other state  $|\phi\rangle$ .

What does Eq. (20.2) mean? We *define* it this way. If you multiply the equation by  $\langle i |$  and expand  $|\psi\rangle$  according to Eq. (20.1), you get

$$\langle i | \phi \rangle = \sum_j \langle i | \hat{A} | j \rangle \langle j | \psi \rangle. \quad (20.3)$$

(The states  $|j\rangle$  are from the same set as  $|i\rangle$ .) This is now just an algebraic equation. The numbers  $\langle i | \phi \rangle$  give the amount of each base state you will find in  $|\phi\rangle$ , and it is given in terms of a linear superposition of the amplitudes  $\langle j | \psi \rangle$  that you find

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$|\psi\rangle$  in each base state. The numbers  $\langle i | \hat{A} | j \rangle$  are just the coefficients which tell how much of  $\langle j | \psi \rangle$  goes into each sum. The operator  $\hat{A}$  is described numerically by the set of numbers, or “matrix,”

$$A_{ij} \equiv \langle i | \hat{A} | j \rangle. \quad (20.4)$$

So Eq. (20.2) is a high-class way of writing Eq. (20.3). Actually it is a little more than that; something more is implied. In Eq. (20.2) we do not make any reference to a set of base states. Equation (20.3) is an image of Eq. (20.2) in terms of some set of base states. But, as you know, you may use any set you wish. And this idea is implied in Eq. (20.2). The operator way of writing avoids making any particular choice. Of course, when you want to get definite you have to choose *some* set. When you make your choice, you use Eq. (20.3). So the *operator* equation (20.2) is a more abstract way of writing the *algebraic* equation (20.3). It's similar to the difference between writing

$$\mathbf{c} = \mathbf{a} \times \mathbf{b}$$

instead of

$$c_x = a_y b_z - a_z b_y,$$

$$c_y = a_z b_x - a_x b_z,$$

$$c_z = a_x b_y - a_y b_x.$$

The first way is much handier. When you want *results*, however, you will eventually have to give the components with respect to some set of axes. Similarly, if you want to be able to say what you really mean by  $\hat{A}$ , you will have to be ready to give the matrix  $A_{ij}$  in terms of *some* set of base states. So long as you have in mind some set  $A_{ij}$ , Eq. (20.2) means just the same as Eq. (20.3). (You should remember also that once you know a matrix for one particular set of base states you can always calculate the corresponding matrix that goes with any other base. You can transform the matrix from one “representation” to another.)

The operator equation in (20.2) also allows a new way of thinking. If we imagine some operator  $\hat{A}$ , we can use it with any state  $|\psi\rangle$  to create a new state  $\hat{A}|\psi\rangle$ . Sometimes a “state” we get this way may be very peculiar—it may not represent any *physical* situation we are likely to encounter in nature. (For instance, we may get a state that is not normalized to represent one electron.) In other words, we may at times get “states” that are mathematically artificial. Such artificial “states” may still be useful, perhaps as the mid-point of some calculation.

We have already shown you many examples of quantum-mechanical operators. We have had the rotation operator  $\hat{R}_y(\theta)$  which takes a state  $|\psi\rangle$  and produces a new state, which is the old state as seen in a rotated coordinate system. We have had the parity (or inversion) operator  $\hat{P}$ , which makes a new state by reversing all coordinates. We have had the operators  $\hat{\sigma}_x$ ,  $\hat{\sigma}_y$ , and  $\hat{\sigma}_z$  for spin one-half particles.

The operator  $\hat{J}_z$  was defined in Chapter 17 in terms of the rotation operator for a small angle  $\epsilon$ .

$$\hat{R}_z(\epsilon) = 1 + \frac{i}{\hbar} \epsilon \hat{J}_z. \quad (20.5)$$

This just means, of course, that

$$\hat{R}_z(\epsilon) |\psi\rangle = |\psi\rangle + \frac{i}{\hbar} \epsilon \hat{J}_z |\psi\rangle. \quad (20.6)$$

In this example,  $\hat{J}_z |\psi\rangle$  is  $\hbar/i\epsilon$  times the state you get if you rotate  $|\psi\rangle$  by the small angle  $\epsilon$  and then subtract the original state. It represents a “state” which is the *difference* of two states.

One more example. We had an operator  $\hat{p}_x$ —called the momentum operator ( $x$ -component) defined in an equation like (20.6). If  $\hat{D}_x(L)$  is the operator which

displaces a state along  $x$  by the distance  $L$ , then  $\hat{p}_x$  is defined by

$$\hat{D}_x(\delta) = 1 + \frac{i}{\hbar} \delta \hat{p}_x, \quad (20.7)$$

where  $\delta$  is a small displacement. Displacing the state  $|\psi\rangle$  along  $x$  by a small distance  $\delta$  gives a new state  $|\psi'\rangle$ . We are saying that this new state is the old state plus a small new piece

$$\frac{i}{\hbar} \delta \hat{p}_x |\psi\rangle.$$

The operators we are talking about work on a state vector like  $|\psi\rangle$ , which is an abstract description of a physical situation. They are quite different from *algebraic* operators which work on mathematical functions. For instance,  $d/dx$  is an “operator” that works on  $f(x)$  by changing it to a new function  $f'(x) = df/dx$ . Another example is the algebraic operator  $\nabla^2$ . You can see why the same word is used in both cases, but you should keep in mind that the two kinds of operators are different. A quantum-mechanical operator  $\hat{A}$  does *not* work on an algebraic function, but on a state vector like  $|\psi\rangle$ . Both kinds of operators are used in quantum mechanics and often in similar kinds of equations, as you will see a little later. When you are first learning the subject it is well to keep the distinction always in mind. Later on, when you are more familiar with the subject, you will find that it is less important to keep any sharp distinction between the two kinds of operators. You will, indeed, find that most books generally use the same notation for both!

We’ll go on now and look at some useful things you can do with operators. But first, one special remark. Suppose we have an operator  $\hat{A}$  whose matrix in some base is  $A_{ij} \equiv \langle i | \hat{A} | j \rangle$ . The amplitude that the state  $\hat{A} |\psi\rangle$  is also in some other state  $|\phi\rangle$  is  $\langle \phi | \hat{A} |\psi\rangle$ . Is there some meaning to the complex conjugate of this amplitude? You should be able to show that

$$\langle \phi | \hat{A} |\psi\rangle^* = \langle \psi | \hat{A}^\dagger | \phi \rangle, \quad (20.8)$$

where  $\hat{A}^\dagger$  (read “A dagger”) is an operator whose matrix elements are

$$A_{ij}^\dagger = (A_{ji})^*. \quad (20.9)$$

To get the  $i, j$  element of  $A^\dagger$  you go to the  $j, i$  element of  $\hat{A}$  (the indexes are reversed) and take its complex conjugate. The amplitude that the state  $\hat{A}^\dagger |\phi\rangle$  is in  $|\psi\rangle$  is the complex conjugate of the amplitude that  $\hat{A} |\psi\rangle$  is in  $|\phi\rangle$ . The operator  $\hat{A}^\dagger$  is called the “Hermitian adjoint” of  $\hat{A}$ . Many important operators of quantum mechanics have the special property that when you take the Hermitian adjoint, you get the same operator back. If  $\hat{B}$  is such an operator, then

$$\hat{B}^\dagger = \hat{B},$$

and it is called a “self-adjoint” or “Hermitian,” operator.

## 20-2 Average energies

So far we have reminded you mainly of what you already know. Now we would like to discuss a new question. How would you find the *average* energy of a system—say, an atom? If an atom is in a particular state of definite energy and you measure the energy, you will find a certain energy  $E$ . If you keep repeating the measurement on each one of a whole series of atoms which are all selected to be in the same state, all the measurements will give  $E$ , and the “average” of your measurements will, of course, be just  $E$ .

Now, however, what happens if you make the measurement on some state  $|\psi\rangle$  which is *not* a stationary state? Since the system does not have a definite energy, one measurement would give one energy, the same measurement on another atom in the same state would give a different energy, and so on. What would you get for the average of a whole series of energy measurements?

We can answer the question by projecting the state  $|\psi\rangle$  onto the set of states of definite energy. To remind you that this is a special base set, we'll call the states  $|\eta_i\rangle$ . Each of the states  $|\eta_i\rangle$  has a definite energy  $E_i$ . In this representation,

$$|\psi\rangle = \sum_i C_i |\eta_i\rangle. \quad (20.10)$$

When you make an energy measurement and get some number  $E_i$ , you have found that the system was in the state  $\eta_i$ . But you may get a different number for each measurement. Sometimes you will get  $E_1$ , sometimes  $E_2$ , sometimes  $E_3$ , and so on. The *probability* that you observe the energy  $E_1$  is just the probability of finding the system in the state  $|\eta_1\rangle$ , which is, of course, just the absolute square of the amplitude  $C_1 = \langle\eta_1|\psi\rangle$ . The probability of finding each of the possible energies  $E_i$  is

$$P_i = |C_i|^2. \quad (20.11)$$

How are these probabilities related to the mean value of a whole sequence of energy measurements? Let's imagine that we get a series of measurements like this:  $E_1, E_7, E_{11}, E_9, E_1, E_{10}, E_7, E_2, E_3, E_9, E_6, E_4$ , and so on. We continue for, say, a thousand measurements. When we are finished we add all the energies and divide by one thousand. That's what we mean by the average. There's also a short-cut to adding all the numbers. You can count up how many times you get  $E_1$ , say that is  $N_1$ , and then count up the number of times you get  $E_2$ , call that  $N_2$ , and so on. The sum of all the energies is certainly just

$$N_1 E_1 + N_2 E_2 + N_3 E_3 + \cdots = \sum_i N_i E_i.$$

The average energy is this sum divided by the total number of measurements which is just the sum of all the  $N_i$ 's, which we can call  $N$ ;

$$E_{\text{av}} = \frac{\sum_i N_i E_i}{N}. \quad (20.12)$$

We are almost there. What we *mean* by the probability of something happening is just the number of times we expect it to happen divided by the total number of tries. The ratio  $N_i/N$  should—for large  $N$ —be very near to  $P_i$ , the probability of finding the state  $|\eta_i\rangle$ , although it will not be exactly  $P_i$  because of the statistical fluctuations. Let's write the predicted (or "expected") average energy as  $\langle E \rangle_{\text{av}}$ ; then we can say that

$$\langle E \rangle_{\text{av}} = \sum_i P_i E_i. \quad (20.13)$$

The same arguments apply for any measurement. The average value of a measured quantity  $A$  should be equal to

$$\langle A \rangle_{\text{av}} = \sum_i P_i A_i,$$

where  $A_i$  are the various possible values of the observed quantity, and  $P_i$  is the probability of getting that value.

Let's go back to our quantum-mechanical state  $|\psi\rangle$ . It's average energy is

$$\langle E \rangle_{\text{av}} = \sum_i |C_i|^2 E_i = \sum_i C_i^* C_i E_i. \quad (20.14)$$

Now watch this trickery! First, we write the sum as

$$\sum_i \langle\psi|\eta_i\rangle E_i \langle\eta_i|\psi\rangle. \quad (20.15)$$

Next we treat the left-hand  $\langle\psi|$  as a common "factor." We can take this factor out of the sum, and write it as

$$\langle\psi| \left\{ \sum_i |\eta_i\rangle E_i \langle\eta_i|\psi\rangle \right\}.$$

This expression has the form

$$\langle \psi | \phi \rangle,$$

where  $|\phi\rangle$  is some “cooked-up” state defined by

$$|\phi\rangle = \sum_i |\eta_i\rangle E_i \langle \eta_i | \psi \rangle. \quad (20.16)$$

It is, in other words, the state you get if you take each base state  $|\eta_i\rangle$  in the amount  $E_i \langle \eta_i | \psi \rangle$ .

Now remember what we mean by the states  $|\eta_i\rangle$ . They are supposed to be the stationary states—by which we mean that for each one,

$$\hat{H} |\eta_i\rangle = E_i |\eta_i\rangle.$$

Since  $E_i$  is just a number, the right-hand side is the same as  $|\eta_i\rangle E_i$ , and the sum in Eq. (20.16) is the same as

$$\sum_i \hat{H} |\eta_i\rangle \langle \eta_i | \psi \rangle.$$

Now  $i$  appears only in the famous combination that contracts to unity, so

$$\sum_i \hat{H} |\eta_i\rangle \langle \eta_i | \psi \rangle = \hat{H} \sum_i |\eta_i\rangle \langle \eta_i | \psi \rangle = \hat{H} |\psi\rangle.$$

Magic! Equation (20.16) is the same as

$$|\phi\rangle = \hat{H} |\psi\rangle. \quad (20.17)$$

The average energy of the state  $|\psi\rangle$  can be written very prettily as

$$\langle E \rangle_{\text{av}} = \langle \psi | \hat{H} | \psi \rangle. \quad (20.18)$$

To get the average energy you operate on  $|\psi\rangle$  with  $\hat{H}$ , and then multiply by  $\langle \psi |$ . A simple result.

Our new formula for the average energy is not only pretty. It is also useful, because now we don't need to say anything about any particular set of base states. We don't even have to know all of the possible energy levels. When we go to calculate, we'll need to describe our state in terms of *some* set of base states, but if we know the Hamiltonian matrix  $H_{ij}$  for *that* set we can get the average energy. Equation (19.18) says that for *any* set of base states  $|i\rangle$ , the average energy can be calculated from

$$\langle E \rangle_{\text{av}} = \sum_{ij} \langle \psi | i \rangle \langle i | \hat{H} | j \rangle \langle j | \psi \rangle, \quad (20.19)$$

where the amplitudes  $\langle i | \hat{H} | j \rangle$  are just the elements of the matrix  $H_{ij}$ .

Let's check this result for the special case that the states  $|i\rangle$  are the definite energy states. For them,  $\hat{H} |j\rangle = E_j |j\rangle$ , so  $\langle i | \hat{H} | j \rangle = E_j \delta_{ij}$  and

$$\langle E \rangle_{\text{av}} = \sum_{ij} \langle \psi | i \rangle E_i \delta_{ij} \langle j | \psi \rangle = \sum_i E_i \langle \psi | i \rangle \langle i | \psi \rangle,$$

which is right.

Equation (20.19) can, incidentally, be extended to other physical measurements which you can express as an operator. For instance,  $\hat{L}_z$  is the operator of the  $z$ -component of the angular momentum  $L$ . The average of the  $z$ -component for the state  $|\psi\rangle$  is

$$\langle L_z \rangle_{\text{av}} = \langle \psi | \hat{L}_z | \psi \rangle.$$

One way to prove it is to think of some situation in which the energy is proportional to the angular momentum. Then all the arguments go through in the same way.

In summary, if a physical observable  $A$  is related to a suitable quantum-mechanical operator  $\hat{A}$ , the average value of  $A$  for the state  $|\psi\rangle$  is given by

$$\langle A \rangle_{\text{av}} = \langle \psi | \hat{A} | \psi \rangle. \quad (20.20)$$

By this we mean that

$$A_{\text{av}} = \langle \psi | \phi \rangle, \quad (20.21)$$

with

$$|\phi\rangle = \hat{A} |\psi\rangle. \quad (20.22)$$

### 20-3 The average energy of an atom

Suppose we want the average energy of an atom in a state described by a wave function  $\psi(\mathbf{r})$ ; How do we find it? Let's first think of a one-dimensional situation with a state  $|\psi\rangle$  defined by the amplitude  $\langle x | \psi \rangle = \psi(x)$ . We are asking for the special case of Eq. (20.19) applied to the coordinate representation. Following our usual procedure, we replace the states  $|i\rangle$  and  $|j\rangle$  by  $|x\rangle$  and  $|x'\rangle$ , and change the sums to integrals. We get

$$\langle E \rangle_{\text{av}} = \int \int \langle \psi | x \rangle \langle x | \hat{H} | x' \rangle \langle x' | \psi \rangle dx dx'. \quad (20.23)$$

This integral can, if we wish, be written in the following way:

$$\int \langle \psi | x \rangle \langle x | \phi \rangle dx, \quad (20.24)$$

with

$$\langle x | \phi \rangle = \int \langle x | \hat{H} | x' \rangle \langle x' | \psi \rangle dx'. \quad (20.25)$$

The integral over  $x'$  in (20.25) is the same one we had in Chapter 16—see Eq. (16.50) and Eq. (16.52)—and is equal to

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

We can therefore write

$$\langle x | \phi \rangle = \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} \psi(x). \quad (20.26)$$

Remember that  $\langle \psi | x \rangle = \langle x | \psi \rangle^* = \psi^*(x)$ ; using this equality, the average energy in Eq. (20.23) can be written as

$$\langle E \rangle_{\text{av}} = \int \psi^*(x) \left\{ -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V \right\} \psi(x) dx. \quad (20.27)$$

Given a wave function  $\psi(x)$ , you can get the average energy by doing this integral. You can begin to see how we can go back and forth from the state-vector ideas to the wave-function ideas.

The quantity in the braces of Eq. (20.27) is an *algebraic* operator.† We will write it as  $\hat{\mathcal{C}}$

$$\hat{\mathcal{C}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V.$$

With this notation Eq. (20.23) becomes

$$\langle E \rangle_{\text{av}} = \int \psi^*(x) \hat{\mathcal{C}} \psi(x) dx. \quad (20.28)$$

The algebraic operator  $\hat{\mathcal{C}}$  defined here is, of course, not identical to the quantum-mechanical operator  $\hat{H}$ . The new operator works on a function of position  $\psi(x) = \langle x | \psi \rangle$  to give a new function of  $x$ ,  $\phi(x) = \langle x | \phi \rangle$ ; while  $\hat{H}$

† The “operator”  $V(x)$  means “multiply by  $V(x)$ .”

operates on a state vector  $|\psi\rangle$  to give another state vector  $|\phi\rangle$ , without implying the coordinate representation or any particular representation at all. Nor is  $\hat{\mathcal{C}}$  strictly the same as  $\hat{H}$  even in the coordinate representation. If we choose to work in the coordinate representation, we would interpret  $\hat{H}$  in terms of a matrix  $\langle x | \hat{H} | x' \rangle$  which depends somehow on the two "indices"  $x$  and  $x'$ ; that is, we expect—according to Eq. (20.25)—that  $\langle x | \phi \rangle$  is related to all the amplitudes  $\langle x | \psi \rangle$  by an integration. On the other hand, we find that  $\hat{\mathcal{C}}$  is a differential operator. We have already worked out in Section 16-5 the connection between  $\langle x | \hat{H} | x' \rangle$  and the algebraic operator  $\hat{\mathcal{C}}$ .

We should make one qualification on our results. We have been assuming that the amplitude  $\psi(x) = \langle x | \psi \rangle$  is normalized. By this we mean that the scale has been chosen so that

$$\int |\psi(x)|^2 dx = 1;$$

so the probability of finding the electron *somewhere* is unity. If you should choose to work with a  $\psi(x)$  which is not normalized you should write

$$\langle E \rangle_{av} = \frac{\int \psi^*(x) \hat{\mathcal{C}} \psi(x) dx}{\int \psi^*(x) \psi(x) dx}. \quad (20.29)$$

It's the same thing.

Notice the similarity in form between Eq. (20.28) and Eq. (20.18). These two ways of writing the same result appear often when you work with the  $x$ -representation. You can go from the first form to the second with any  $\hat{A}$  which is a *local* operator, where a local operator is one which in the integral

$$\int \langle x | \hat{A} | x' \rangle \langle x' | \psi \rangle dx'$$

can be written as  $\hat{\alpha} \psi(x)$ , where  $\hat{\alpha}$  is a differential algebraic operator. There are, however, operators for which this is not true. For them you must work with the basic equations in (20.21) and (20.22).

You can easily extend the derivation to three dimensions. The result is that†

$$\langle E \rangle_{av} = \int \psi^*(\mathbf{r}) \hat{\mathcal{C}} \psi(\mathbf{r}) d \text{Vol}, \quad (20.30)$$

with

$$\hat{\mathcal{C}} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}), \quad (20.31)$$

and with the understanding that

$$\int |\psi|^2 d \text{Vol} = 1. \quad (20.32)$$

The same equations can be extended to systems with several electrons in a fairly obvious way, but we won't bother to write down the results.

With Eq. (20.30) we can calculate the average energy of an atomic state even without knowing its energy levels. All we need is the wave function. It's an important law. We'll tell you about one interesting application. Suppose you want to know the ground-state energy of some system—say the helium atom, but it's too hard to solve Schrödinger's equation for the wave function, because there are too many variables. Suppose, however, that you take a guess at the wave function—pick any function you like—and calculate the average energy. That is, you use Eq. (20.29)—generalized to three dimensions—to find what the average energy would be if the atom were really in the state described by this wave function. This energy will certainly be higher than the ground-state energy which is the lowest

† We write  $d \text{Vol}$  for the element of volume. It is, of course, just  $dx dy dz$ , and the integral goes from  $-\infty$  to  $+\infty$  in all three coordinates.

possible energy the atom can have.† Now pick another function and calculate its average energy. If it is lower than your first choice you are getting closer to the true ground-state energy. If you keep on trying all sorts of artificial states you will be able to get lower and lower energies, which come closer and closer to the ground-state energy. If you are clever, you will try some functions which have a few adjustable parameters. When you calculate the energy it will be expressed in terms of these parameters. By varying the parameters to give the lowest possible energy, you are trying out a whole class of functions at once. Eventually you will find that it is harder and harder to get lower energies and you will begin to be convinced that you are fairly close to the lowest possible energy. The helium atom has been solved in just this way—not by solving a differential equation, but by making up a special function with a lot of adjustable parameters which are eventually chosen to give the lowest possible value for the average energy.

#### 20-4 The position operator

What is the average value of the position of an electron in an atom? For any particular state  $|\psi\rangle$  what is the average value of the coordinate  $x$ ? We'll work in one dimension and let you extend the ideas to three dimensions or to systems with more than one particle. We have a state described by  $\psi(x)$ , and we keep measuring  $x$  over and over again. What is the average? It is

$$\int xP(x) dx,$$

where  $P(x)$  is the probability of finding the electron in a little element  $dx$  at  $x$ . Suppose the probability density  $P(x)$  varies with  $x$  as shown in Fig. 20-1. The electron is most likely to be found near the peak of the curve. The average value of  $x$  is also somewhere near the peak. It is, in fact, just the center of gravity of the area under the curve.

We have seen earlier that  $P(x)$  is just  $|\psi(x)|^2 = \psi^*(x)\psi(x)$ , so we can write the average of  $x$  as

$$\langle x \rangle_{av} = \int \psi^*(x)x\psi(x) dx. \quad (20.33)$$

Our equation for  $\langle x \rangle_{av}$  has the same form as Eq. (20.33). For the average energy, the energy operator  $\hat{\mathcal{E}}$  appears between the two  $\psi$ 's, for the average position there is just  $x$ . (If you wish you can consider  $x$  to be the algebraic operator "multiply by  $x$ .") We can carry the parallelism still further, expressing the average position in a form which corresponds to Eq. (20.18). Suppose we just write

$$\langle x \rangle_{av} = \langle \psi | \alpha \rangle \quad (20.34)$$

with

$$|\alpha\rangle = \hat{x} |\psi\rangle, \quad (20.35)$$

and then see if we can find the operator  $\hat{x}$  which generates the state  $|\alpha\rangle$ , which will make Eq. (20.34) agree with Eq. (20.33). That is, we must find a  $|\alpha\rangle$ , so that

$$\langle \psi | \alpha \rangle = \langle x \rangle_{av} = \int \langle \psi | x \rangle x \langle x | \psi \rangle dx. \quad (20.36)$$

First, let's expand  $\langle \psi | \phi \rangle$  in the  $x$ -representation. It is

$$\langle \psi | \alpha \rangle = \int \langle \psi | x \rangle \langle x | \alpha \rangle dx. \quad (20.37)$$

Now compare the integrals in the last two equations. You see that in the  $x$ -representation

$$\langle x | \alpha \rangle = x \langle x | \psi \rangle. \quad (20.38)$$

† You can also look at it this way. Any function (that is, state) you choose can be written as a linear combination of the base states which are definite energy states. Since in this combination there is a mixture of higher energy states in with the lowest energy state, the average energy will be higher than the ground-state energy.

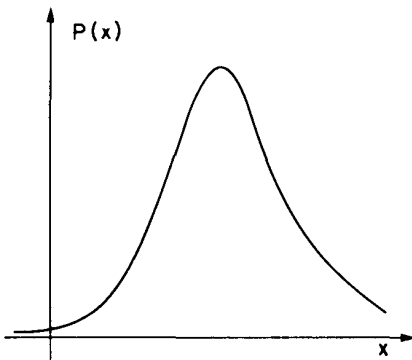


Fig. 20-1. A curve of probability density representing a localized particle.



Operating on  $|\psi\rangle$  with  $\hat{x}$  to get  $|\alpha\rangle$  is equivalent to multiplying  $\psi(x) = \langle x|\psi\rangle$  by  $x$  to get  $\alpha(x) = \langle x|\alpha\rangle$ . We have a definition of  $\hat{x}$  in the coordinate representation.†

[We have not bothered to try to get the  $x$ -representation of the matrix of the operator  $\hat{x}$ . If you are ambitious you can try to show that

$$\langle x|\hat{x}|x'\rangle = x\delta(x-x'). \quad (20.39)$$

You can then work out the amusing result that

$$\hat{x}|x\rangle = x|x\rangle. \quad (20.40)$$

The operator  $\hat{x}$  has the interesting property that when it works on the base states  $|x\rangle$  it is equivalent to multiplying by  $x$ .]

Do you want to know the average value of  $x^2$ ? It is

$$\langle x^2 \rangle_{\text{av}} = \int \psi^*(x)x^2\psi(x) dx. \quad (20.41)$$

Or, if you prefer you can write

$$\langle x^2 \rangle_{\text{av}} = \langle \psi|\alpha'\rangle$$

with

$$|\alpha'\rangle = \hat{x}^2|\psi\rangle. \quad (20.42)$$

By  $\hat{x}^2$  we mean  $\hat{x}\hat{x}$ —the two operators are used one after the other. With the second form you can calculate  $\langle x^2 \rangle_{\text{av}}$  using any representation (base-states) you wish. If you want the average of  $x^n$ , or of any polynomial in  $x$ , you can see how to get it.

## 20-5 The momentum operator

Now we would like to calculate the mean *momentum* of an electron—again, we'll stick to one dimension. Let  $P(p) dp$  be the probability that a measurement will give a momentum between  $p$  and  $p + dp$ . Then

$$\langle p \rangle_{\text{av}} = \int p P(p) dp. \quad (20.43)$$

Now we let  $\langle p|\psi\rangle$  be the amplitude that the state  $|\psi\rangle$  is in a definite momentum state  $|p\rangle$ . This is the same amplitude we called  $\langle \text{mom } p|\psi\rangle$  in Section 16-3 and is a function of  $p$  just as  $\langle x|\psi\rangle$  is a function of  $x$ . There we chose to normalize the amplitude so that

$$P(p) = \frac{1}{2\pi\hbar} |\langle p|\psi\rangle|^2. \quad (20.44)$$

We have, then,

$$\langle p \rangle_{\text{av}} = \int \langle \psi|p\rangle p \langle p|\psi\rangle \frac{dp}{2\pi\hbar}. \quad (20.45)$$

The form is quite similar to what we had for  $\langle x \rangle_{\text{av}}$ .

If we want, we can play exactly the same game we did with  $\langle x \rangle_{\text{av}}$ . First, we can write the integral above as

$$\int \langle \psi|p\rangle \langle p|\beta\rangle \frac{dp}{2\pi\hbar}. \quad (20.46)$$

You should now recognize this equation as just the expanded form of the amplitude  $\langle \psi|\beta\rangle$ —expanded in terms of the base states of definite momentum. From Eq.

† Equation (20.38) does *not* mean that  $|\alpha\rangle = x|\psi\rangle$ . You cannot “factor out” the  $\langle x|$ , because the multiplier  $x$  in front of  $\langle x|\psi\rangle$  is a number which is different for each state  $\langle x|$ . It is the value of the coordinate of the electron in the state  $|x\rangle$ . See Eq. (20.40).

(20.45) the state  $|\beta\rangle$  is defined *in the momentum representation* by

$$\langle p | \beta \rangle = p \langle p | \psi \rangle \quad (20.47)$$

That is, we can now write

$$\langle p \rangle_{\text{av}} = \langle \psi | \beta \rangle \quad (20.48)$$

with

$$|\beta\rangle = \hat{p} |\psi\rangle, \quad (20.49)$$

where the operator  $\hat{p}$  is defined in terms of the  $p$ -representation by Eq. (20.47).

[Again, you can if you wish show that the matrix form of  $\hat{p}$  is

$$\langle p | \hat{p} | p' \rangle = p \delta(p - p'), \quad (20.50)$$

and that

$$\hat{p} | p \rangle = p | p \rangle. \quad (20.51)$$

It works out the same as for  $x$ .]

Now comes an interesting question. We can write  $\langle p \rangle_{\text{av}}$  as we have done in Eqs. (20.45) and (20.48), and we know the meaning of the operator  $\hat{p}$  *in the momentum representation*. But how should we interpret  $\hat{p}$  in the *coordinate* representation? That is what we will need to know if we have some wave function  $\psi(x)$ , and we want to compute its average momentum. Let's make clear what we mean. If we start by saying that  $\langle p \rangle_{\text{av}}$  is given by Eq. (20.48), we can expand that equation in terms of the  $p$ -representation to get back to Eq. (20.45). If we are given the  $p$ -description of the state—namely the amplitude  $\langle p | \psi \rangle$ , which is an algebraic function of the momentum  $p$ —we can get  $\langle p | \phi \rangle$  from Eq. (20.47) and proceed to evaluate the integral. The question now is: What do we do if we are given a description of the state in the  $x$ -representation, namely the wave function  $\psi(x) = \langle x | \psi \rangle$ ?

Well, let's start by expanding Eq. (20.48) in the  $x$ -representation. It is

$$\langle p \rangle_{\text{av}} = \int \langle \psi | x \rangle \langle x | \beta \rangle dx. \quad (20.52)$$

Now, however, we need to know what the state  $|\beta\rangle$  is in the  $x$ -representation. If we can find it, we can carry out the integral. So our problem is to find the function  $\beta(x) = \langle x | \beta \rangle$ .

We can find it in the following way. In Section 16-3 we saw how  $\langle p | \beta \rangle$  was related to  $\langle x | \beta \rangle$ . According to Eq. (16.24),

$$\langle p | \beta \rangle = \int e^{-ipx/\hbar} \langle x | \beta \rangle dx. \quad (20.53)$$

If we know  $\langle p | \beta \rangle$  we can solve this equation for  $\langle x | \beta \rangle$ . What we want, of course, is to express the result somehow in terms of  $\psi(x) = \langle x | \psi \rangle$ , which we are assuming to be known. Suppose we start with Eq. (20.47) and again use Eq. (16.24) to write

$$\langle p | \beta \rangle = p \langle p | \psi \rangle = p \int e^{-ipx/\hbar} \psi(x) dx. \quad (20.54)$$

Since the integral is over  $x$  we can put the  $p$  inside the integral and write

$$\langle p | \beta \rangle = \int e^{-ipx/\hbar} p \psi(x) dx. \quad (20.55)$$

Compare this with (20.53). You would say that  $\langle x | \beta \rangle$  is equal to  $p\psi(x)$ . No, No! The wave function  $\langle x | \beta \rangle = \beta(x)$  can depend only on  $x$ —not on  $p$ . That's the whole problem.

However, some ingenious fellow discovered that the integral in (20.55) could be integrated by parts. The derivative of  $e^{-ipx/\hbar}$  with respect to  $x$  is  $(-i/\hbar)pe^{-ipx/\hbar}$ , so the integral in (20.55) is equivalent to

$$-\frac{\hbar}{i} \int \frac{d}{dx} (e^{-ipx/\hbar}) \psi(x) dx.$$

If we integrate by parts, it becomes

$$-\frac{\hbar}{i} [e^{-ipx/\hbar} \psi(x)]_{-\infty}^{+\infty} + \frac{\hbar}{i} \int e^{-ipx/\hbar} \frac{d\psi}{dx} dx.$$

So long as we are considering bound states, so that  $\psi(x)$  goes to zero at  $x = \pm \infty$ , the bracket is zero and we have

$$\langle p | \beta \rangle = \frac{\hbar}{i} \int e^{-ipx/\hbar} \frac{d\psi}{dx} dx. \quad (20.56)$$

Now compare this result with Eq. (20.53). You see that

$$\langle x | \beta \rangle = \frac{\hbar}{i} \frac{d}{dx} \psi(x). \quad (20.57)$$

We have the necessary piece to be able to complete Eq. (20.52). The answer is

$$\langle p \rangle_{\text{av}} = \int \psi^*(x) \frac{\hbar}{i} \frac{d}{dx} \psi(x) dx. \quad (20.58)$$

We have found how Eq. (20.48) looks in the coordinate representation.

Now you should begin to see an interesting pattern developing. When we asked for the average energy of the state  $|\psi\rangle$  we said it was

$$\langle E \rangle_{\text{av}} = \langle \psi | \phi \rangle, \quad \text{with } |\phi\rangle = \hat{H} |\psi\rangle.$$

The same thing is written in the coordinate world as

$$\langle E \rangle_{\text{av}} = \int \psi^*(x) \phi(x) dx \quad \text{with } \phi(x) = \hat{\mathcal{H}} \psi(x).$$

Here  $\hat{\mathcal{H}}$  is an *algebraic* operator which works a function of  $x$ . When we asked about the average value of  $x$ , we found that it could also be written

$$\langle x \rangle_{\text{av}} = \langle \psi | \alpha \rangle, \quad \text{with } |\alpha\rangle = \hat{x} |\psi\rangle.$$

In the coordinate world the corresponding equations are

$$\langle x \rangle_{\text{av}} = \int \psi^*(x) \alpha(x) dx, \quad \text{with } \alpha(x) = x\psi(x).$$

When we asked about the average value of  $p$ , we wrote

$$\langle p \rangle_{\text{av}} = \langle \psi | \beta \rangle, \quad \text{with } |\beta\rangle = \hat{p} |\psi\rangle.$$

In the coordinate world the equivalent equations were

$$\langle p \rangle_{\text{av}} = \int \psi(x) \beta(x) dx, \quad \text{with } \beta(x) = \frac{\hbar}{i} \frac{d}{dx} \psi(x).$$

In each of our three examples we start with the state  $|\psi\rangle$  and produce another (hypothetical) state by a *quantum-mechanical* operator. In the coordinate representation we generate the corresponding wave function by operating on the wave function  $\psi(x)$  with an *algebraic* operator. There are the following one-to-one correspondences (for one-dimensional problems):

$$\begin{aligned} \hat{H} &\rightarrow \hat{\mathcal{H}} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x), \\ \hat{x} &\rightarrow x, \\ \hat{p}_x &\rightarrow \hat{\mathcal{P}}_x = \frac{\hbar}{i} \frac{\partial}{\partial x}. \end{aligned} \quad (20.59)$$

Table 20-1

Physical Quantity	Operator	Coordinate Form
Energy	$\hat{H}$	$\hat{\mathcal{H}} = -\frac{\hbar^2}{2m}\nabla^2 + V(r)$
Position	$\hat{x}$	$x$
	$\hat{y}$	$y$
	$\hat{z}$	$z$
Momentum	$\hat{p}_x$	$\hat{\mathcal{P}}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$
	$\hat{p}_y$	$\hat{\mathcal{P}}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}$
	$\hat{p}_z$	$\hat{\mathcal{P}}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$

In this list, we have introduced the symbol  $\hat{\mathcal{P}}_x$  for the algebraic operator  $(\hbar/i)\partial/\partial x$ :

$$\hat{\mathcal{P}}_x = \frac{\hbar}{i}\frac{\partial}{\partial x}, \quad (20.60)$$

and we have inserted the  $x$  subscript on  $\hat{\mathcal{P}}$  to remind you that we have been working only with the  $x$ -component of momentum.

You can easily extend the results to three dimensions. For the other components of the momentum,

$$\begin{aligned} \hat{p}_y &\rightarrow \hat{\mathcal{P}}_y = \frac{\hbar}{i}\frac{\partial}{\partial y}, \\ \hat{p}_z &\rightarrow \hat{\mathcal{P}}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}. \end{aligned}$$

If you want, you can even think of an operator of the *vector* momentum and write

$$\hat{\mathbf{p}} \rightarrow \hat{\mathcal{P}} = \frac{\hbar}{i}\left(\mathbf{e}_x\frac{\partial}{\partial x} + \mathbf{e}_y\frac{\partial}{\partial y} + \mathbf{e}_z\frac{\partial}{\partial z}\right),$$

where  $\mathbf{e}_x$ ,  $\mathbf{e}_y$ , and  $\mathbf{e}_z$  are the unit vectors in the three directions. It looks even more elegant if we write

$$\hat{\mathbf{p}} \rightarrow \hat{\mathcal{P}} = \frac{\hbar}{i}\nabla. \quad (20.61)$$

Our general result is that for at least some quantum-mechanical operators, there are corresponding algebraic operators in the coordinate representation. We summarize our results so far—extended to three dimensions—in Table 20-1. For each operator we have the two equivalent forms:‡

$$|\phi\rangle = \hat{A}|\psi\rangle \quad (20.62)$$

or

$$\phi(\mathbf{r}) = \hat{\mathcal{A}}\psi(\mathbf{r}). \quad (20.63)$$

We will now give a few illustrations of the use of these ideas. The first one is just to point out the relation between  $\hat{\mathcal{P}}$  and  $\hat{\mathcal{H}}$ . If we use  $\hat{\mathcal{P}}_x$  twice, we get

$$\hat{\mathcal{P}}_x\hat{\mathcal{P}}_x = -\hbar^2\frac{\partial^2}{\partial x^2}.$$

‡ In many books the same symbol is used for  $\hat{A}$  and  $\hat{\mathcal{A}}$ , because they both stand for the same physics, and because it is convenient not to have to write different kinds of letters. You can usually tell which one is intended by the context

This means that we can write the equality

$$\hat{\mathcal{H}} = \frac{1}{2m} \{ \hat{p}_x \hat{p}_x + \hat{p}_y \hat{p}_y + \hat{p}_z \hat{p}_z \} + V(\mathbf{r}).$$

Or, using the vector notation,

$$\hat{\mathcal{H}} = \frac{1}{2m} \hat{\mathbf{p}} \cdot \hat{\mathbf{p}} + V(\mathbf{r}). \quad (20.64)$$

(In an algebraic operator, any term without the operator symbol ( $\hat{\quad}$ ) means just a straight multiplication.) This equation is nice because it's easy to remember if you haven't forgotten your classical physics. Everyone knows that the energy is (nonrelativistically) just the kinetic energy  $p^2/2m$  plus the potential energy, and  $\hat{\mathcal{H}}$  is the operator of the total energy.

This result has impressed people so much that they try to teach students all about classical physics before quantum mechanics. (We think differently!) But such parallels are often misleading. For one thing, when you have operators, the *order* of various factors is important; but that is not true for the factors in a classical equation.

In Chapter 17 we defined an operator  $\hat{p}_x$  in terms of the displacement operator  $\hat{D}_x$  by [see Eq. (17.27)]

$$|\psi'\rangle = \hat{D}_x(\delta) |\psi\rangle = \left( 1 + \frac{i}{\hbar} \hat{p}_x \delta \right) |\psi\rangle, \quad (20.65)$$

where  $\delta$  is a *small* displacement. We should show you that this is equivalent to our new definition. According to what we have just worked out, this equation should mean the same as

$$\psi'(x) = \psi(x) + \frac{\partial \psi}{\partial x} \delta$$

But the right-hand side is just the Taylor expansion of  $\psi(x + \delta)$ , which is certainly what you get if you displace the state to the left by  $\delta$  (or shift the coordinates to the right by the same amount). Our two definitions of  $\hat{p}$  agree!

Let's use this fact to show something else. Suppose we have a bunch of particles which we label 1, 2, 3, . . . , in some complicated system. (To keep things simple we'll stick to one dimension.) The wave function describing the state is a function of all the coordinates  $x_1, x_2, x_3, \dots$ . We can write it as  $\psi(x_1, x_2, x_3, \dots)$ . Now displace the system (to the left) by  $\delta$ . The new wave function

$$\psi'(x_1, x_2, x_3, \dots) = \psi(x_1 + \delta, x_2 + \delta, x_3 + \delta, \dots)$$

can be written as

$$\psi'(x_1, x_2, x_3, \dots) = \psi(x_1, x_2, x_3, \dots) + \left\{ \delta \frac{\partial \psi}{\partial x_1} + \delta \frac{\partial \psi}{\partial x_2} + \delta \frac{\partial \psi}{\partial x_3} + \dots \right\}. \quad (20.66)$$

According to Eq. (20.65) the operator of the momentum of the state  $|\psi\rangle$  (let's call it the *total* momentum) is equal to

$$\hat{\mathcal{P}}_{\text{total}} = \frac{\hbar}{i} \left\{ \frac{\partial}{\partial x_1} + \frac{\partial}{\partial x_2} + \frac{\partial}{\partial x_3} + \dots \right\}.$$

But this is just the same as

$$\hat{\mathcal{P}}_{\text{total}} = \hat{\mathcal{P}}_{x_1} + \hat{\mathcal{P}}_{x_2} + \hat{\mathcal{P}}_{x_3} + \dots. \quad (20.67)$$

The operators of momentum obey the rule that the total momentum is the sum of the momenta of all the parts. Everything holds together nicely, and many of the things we have been saying are consistent with each other.

## 20-6 Angular momentum

Let's for fun look at another operation—the operation of orbital angular momentum. In Chapter 17 we defined an operator  $\hat{J}_z$  in terms of  $\hat{R}_z(\varphi)$ , the operator of a rotation by the angle  $\varphi$  about the  $z$ -axis. We consider here a system described simply by a single wave function  $\psi(\mathbf{r})$ , which is a function of coordinates only, and does not take into account the fact that the electron may have its spin either up or down. That is, we want for the moment to disregard *intrinsic* angular momentum and think about only the *orbital* part. To keep the distinction clear, we'll call the orbital operator  $\hat{L}_z$ , and define it in terms of the operator of a rotation by an infinitesimal angle  $\epsilon$  by

$$\hat{R}_z(\epsilon)|\psi\rangle = \left(1 + \frac{i}{\hbar}\epsilon\hat{L}_z\right)|\psi\rangle.$$

(Remember, this definition applies only to a state  $|\psi\rangle$  which has no internal spin variables, but depends only on the coordinates  $\mathbf{r} = x, y, z$ ) If we look at the state  $|\psi\rangle$  in a new coordinate system, rotated about the  $z$ -axis by the small angle  $\epsilon$ , we see a new state

$$|\psi'\rangle = \hat{R}_z(\epsilon)|\psi\rangle.$$

If we choose to describe the state  $|\psi\rangle$  in the coordinate representation—that is, by its wave function  $\psi(\mathbf{r})$ , we would expect to be able to write

$$\psi'(\mathbf{r}) = \left(1 + \frac{i}{\hbar}\epsilon\hat{\mathcal{L}}_z\right)\psi(\mathbf{r}). \quad (20.68)$$

What is  $\hat{\mathcal{L}}$ ? Well, a point  $P$  at  $x$  and  $y$  in the *new* coordinate system (really  $x'$  and  $y'$ , but we will drop the primes) was formerly at  $x - \epsilon y$  and  $y + \epsilon x$ , as you can see from Fig. 20-2. Since the amplitude for the electron to be at  $P$  isn't changed by the rotation of the coordinates we can write

$$\psi'(x, y, z) = \psi(x + \epsilon y, y - \epsilon x, z) = \psi(x, y, z) + \epsilon y \frac{\partial \psi}{\partial x} - \epsilon x \frac{\partial \psi}{\partial y}$$

(remembering that  $\epsilon$  is a small angle). This means that

$$\hat{\mathcal{L}}_z = \frac{\hbar}{i} \left( x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right). \quad (20.69)$$

That's our answer. But notice. It is equivalent to

$$\hat{\mathcal{L}}_z = x\hat{\mathcal{P}}_y - y\hat{\mathcal{P}}_x. \quad (20.70)$$

Returning to our quantum-mechanical operators, we can write

$$\hat{L}_z = x\hat{p}_y - y\hat{p}_x. \quad (20.71)$$

This formula is easy to remember because it looks like the familiar formula of classical mechanics; it is the  $z$ -component of

$$\mathbf{L} = \mathbf{r} \times \mathbf{p}. \quad (20.72)$$

One of the fun parts of this operator business is that many classical equations get carried over into a quantum-mechanical form. Which ones don't? There had better be some that don't come out right, because if everything did, then there would be nothing different about quantum mechanics. There would be no new physics. Here is one equation which is different. In classical physics

$$xp_x - p_x x = 0.$$

What is it in quantum mechanics?

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = ?$$

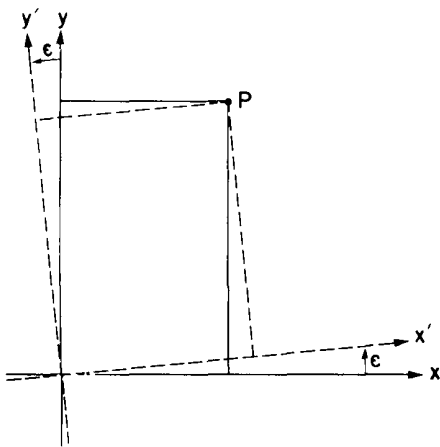


Fig. 20-2. Rotation of the axes around the  $z$ -axis by the small angle  $\epsilon$ .

Let's work it out in the  $x$ -representation. So that we'll know what we are doing we put in some wave function  $\psi(x)$ . We have

$$x\mathcal{P}_x\psi(x) - \hat{\mathcal{P}}_x x\psi(x),$$

or

$$x \frac{\hbar}{i} \frac{\partial}{\partial x} \psi(x) - \frac{\hbar}{i} \frac{\partial}{\partial x} x\psi(x).$$

Remember now that the derivatives operate on everything to the right. We get

$$x \frac{\hbar}{i} \frac{\partial \psi}{\partial x} - \frac{\hbar}{i} \psi(x) - \frac{\hbar}{i} x \frac{\partial \psi}{\partial x} = -\frac{\hbar}{i} \psi(x). \quad (20.73)$$

The answer is *not* zero. The whole operation is equivalent simply to multiplication by  $-\hbar/i$ :

$$\hat{x}\hat{p}_x - \hat{p}_x\hat{x} = -\frac{\hbar}{i}. \quad (20.74)$$

If Plank's constant were zero, the classical and quantum results would be the same, and there would be no quantum mechanics to learn!

Incidentally, if any two operators  $\hat{A}$  and  $\hat{B}$ , when taken together like this:

$$\hat{A}\hat{B} - \hat{B}\hat{A},$$

do *not* give zero, we say that "the operators do not commute." And an equation such as (20.74) is called a "commutation rule." You can see that the commutation rule for  $p_x$  and  $y$  is

$$\hat{p}_x\hat{y} - \hat{y}\hat{p}_x = 0.$$

There is another very important commutation rule that has to do with angular momenta. It is

$$\hat{L}_x\hat{L}_y - \hat{L}_y\hat{L}_x = i\hbar\hat{L}_z. \quad (20.75)$$

You can get some practice with  $\hat{x}$  and  $\hat{p}$  operators by proving it for yourself.

It is interesting to notice that operators which do not commute can also occur in classical physics. We have already seen this when we have talked about rotation in space. If you rotate something, such as a book, by  $90^\circ$  around  $x$  and then  $90^\circ$  around  $y$ , you get something different from rotating first by  $90^\circ$  around  $y$  and then by  $90^\circ$  around  $x$ . It is, in fact, just this property of space that is responsible for Eq. (20.75).

## 20-7 The change of averages with time

Now we want to show you something else. How do averages change with time? Suppose for the moment that we have an operator  $\hat{A}$ , which does not itself have time in it in any obvious way. We mean an operator like  $\hat{x}$  or  $\hat{p}$ . (We exclude things like, say, the operator of some external potential that was being varied with time, such as  $V(x, t)$ .) Now suppose we calculate  $\langle A \rangle_{av}$ , in some state  $|\psi\rangle$ , which is

$$\langle A \rangle_{av} = \langle \psi | \hat{A} | \psi \rangle. \quad (20.76)$$

How will  $\langle A \rangle_{av}$  depend on time? Why should it? One reason might be that the operator itself depended explicitly on time—for instance, if it had to do with a time-varying potential like  $V(x, t)$ . But even if the operator does not depend on  $t$ , say, for example, the operator  $\hat{A} = \hat{x}$ , the corresponding average may depend on time. Certainly the average position of a particle could be moving. How does such a motion come out of Eq. (20.76) if  $\hat{A}$  has no time dependence? Well, the state  $|\psi\rangle$  might be changing with time. For nonstationary states we have often shown a time dependence explicitly by writing a state as  $|\psi(t)\rangle$ . We want to show that the rate of change of  $\langle A \rangle_{av}$  is given by a new operator we will call  $\dot{\hat{A}}$ . Remember that  $\hat{A}$  is an operator, so that putting a dot over the  $A$  does not here mean taking

the time derivative, but is just a way of writing a *new* operator  $\hat{A}$  which is defined by

$$\frac{d}{dt} \langle A \rangle_{av} = \langle \psi | \hat{A} | \psi \rangle. \quad (20.77)$$

Our problem is to find the operator  $\hat{A}$ .

First, we know that the rate of change of a state is given by the Hamiltonian. Specifically,

$$i\hbar \frac{d}{dt} | \psi(t) \rangle = \hat{H} | \psi(t) \rangle. \quad (20.78)$$

This is just the abstract way of writing our original definition of the Hamiltonian:

$$i\hbar \frac{dC_i}{dt} = \sum_{j} H_{ij} C_j. \quad (20.79)$$

If we take the complex conjugate of this equation, it is equivalent to

$$-i\hbar \frac{d}{dt} \langle \psi(t) | = \langle \psi(t) | \hat{H}. \quad (20.80)$$

Next, see what happens if we take the derivatives with respect to  $t$  of Eq. (20.76). Since each  $\psi$  depends on  $t$ , we have

$$\frac{d}{dt} \langle A \rangle_{av} = \left( \frac{d}{dt} \langle \psi | \right) \hat{A} | \psi \rangle + \langle \psi | \hat{A} \left( \frac{d}{dt} | \psi \rangle \right). \quad (20.81)$$

Finally, using the two equations in (20.78) and (20.79) to replace the derivatives, we get

$$\frac{d}{dt} \langle A \rangle_{av} = \frac{i}{\hbar} \{ \langle \psi | \hat{H} \hat{A} | \psi \rangle - \langle \psi | \hat{A} \hat{H} | \psi \rangle \}.$$

This equation is the same as

$$\frac{d}{dt} \langle A \rangle_{av} = \frac{i}{\hbar} \langle \psi | (\hat{H} \hat{A} - \hat{A} \hat{H}) | \psi \rangle.$$

Comparing this equation with Eq. (20.77), you see that

$$\hat{A} = \frac{i}{\hbar} (\hat{H} \hat{A} - \hat{A} \hat{H}). \quad (20.82)$$

That is our interesting proposition, and it is true for any operator  $\hat{A}$ .

Incidentally, if the operator  $\hat{A}$  should *itself* be time dependent, we would have had

$$\hat{A} = \frac{i}{\hbar} (\hat{H} \hat{A} - \hat{A} \hat{H}) + \frac{\partial \hat{A}}{\partial t}. \quad (20.83)$$

Let us try out Eq. (20.82) on some example to see whether it really makes sense. For instance, what operator corresponds to  $\hat{x}$ ? We say it should be

$$\hat{x} = \frac{i}{\hbar} (\hat{H} \hat{x} - \hat{x} \hat{H}). \quad (20.84)$$

What is this? One way to find out is to work it through in the coordinate representation using the algebraic operator for  $\hat{\mathcal{H}}$ . In this representation the commutator is

$$\hat{\mathcal{H}}x - x\hat{\mathcal{H}} = \left\{ \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\} x - x \left\{ \frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right\}.$$

If you operate with this on any wave function  $\psi(x)$  and work out all of the derivatives where you can, you end up after a little work with

$$-\frac{\hbar^2}{2m} \frac{d\psi}{dx}.$$



But this is just the same as

$$-i \frac{\hbar}{m} \hat{p}_x \psi,$$

so we find that

$$\hat{H}\hat{x} = \hat{x}\hat{H} = -i \frac{\hbar}{m} p_x \quad (20.85)$$

or that

$$\dot{\hat{x}} = \frac{\hat{p}_x}{m}. \quad (20.86)$$

A pretty result. It means that if the mean value of  $x$  is changing with time the drift of the center of gravity is the same as the mean momentum divided by  $m$ . Exactly like classical mechanics.

Another example. What is the rate of change of the average momentum of a state? Same game. Its operator is

$$\hat{p} = \frac{i}{\hbar} (\hat{H}\hat{p} - \hat{p}\hat{H}). \quad (20.87)$$

Again you can work it out in the  $x$  representation. Remember that  $\hat{p}$  becomes  $d/dx$ , and this means that you will be taking the derivative of the potential energy  $V$  (in the  $\hat{\mathcal{C}}$ )—but only in the second term. It turns out that it is the only term which does not cancel, and you find that

$$\hat{\mathcal{C}}\hat{p} - \hat{p}\hat{\mathcal{C}} = -i\hbar \frac{dV}{dx}$$

or that

$$\hat{p} = - \frac{dV}{dx}. \quad (20.88)$$

Again the classical result. The right-hand side is the force, so we have derived Newton's law! But remember—these are the laws for the *operators* which give the *average* quantities. They do not describe what goes on in detail inside an atom.

Quantum mechanics has the essential difference that  $\hat{p}\hat{x}$  is not equal to  $\hat{x}\hat{p}$ . They differ by a little bit—by the small number  $\hbar$ . But the whole wondrous complications of interference, waves, and all, result from the little fact that  $\hat{x}\hat{p} - \hat{p}\hat{x}$  is not quite zero.

The history of this idea is also interesting. Within a period of a few months in 1926, Heisenberg and Schrödinger independently found correct laws to describe atomic mechanics. Schrödinger invented his wave function  $\psi(x)$  and found his equation. Heisenberg, on the other hand, found that nature could be described by classical equations, except that  $xp - px$  should be equal to  $\hbar/i$ , which he could make happen by defining them in terms of special kinds of matrices. In our language he was using the energy-representation, with its matrices. Both Heisenberg's matrix algebra and Schrödinger's differential equation explained the hydrogen atom. A few months later Schrödinger was able to show that the two theories were equivalent—as we have seen here. But the two different mathematical forms of quantum mechanics were discovered independently.