

## 11.3: Operators and Quantum Mechanics - an Introduction

We have already discussed that the main postulate of quantum mechanics establishes that the state of a quantum mechanical system is specified by a function called *the wavefunction*. The wavefunction is a function of the coordinates of the particle (the position) and time. We often deal with *stationary states*, i.e. states whose energy does not depend on time. For example, at room temperature and in the absence of electromagnetic radiation such as UV light, the energy of the only electron in the hydrogen atom is constant (the energy of the 1s orbital). In this case, all the information about the state of the particle is contained in a time-independent function,  $\psi(\mathbf{r})$ , where  $\mathbf{r}$  is a vector that defines the position of the particle. In spherical coordinates  $\mathbf{r}$  is described in terms of  $r, \theta$  and  $\phi$  (note the difference between  $\mathbf{r}$  and  $r$ ). For example, the wavefunction that describes the 1s orbital is:

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-(r/a_0)} \quad (11.3.1)$$

Notice that in this particular case the wavefunction is independent of  $\theta$  and  $\phi$ . This makes sense because the 1s orbital has spherical symmetry, and therefore the probability of finding the electron in a particular region of space should depend on  $r$  only.

We also discussed one of the postulates of quantum mechanics: the function

$$|\psi(\mathbf{r})|^2 dV = \psi^*(\mathbf{r})\psi(\mathbf{r})dV$$

is the probability that the particle lies in the volume element  $dV$  located at  $\mathbf{r}$ . We will now introduce three additional postulates:

1. Each observable in classical mechanics has an associated operator in quantum mechanics. Examples of observables are position, momentum, kinetic energy, total energy, angular momentum, etc (Table 11.3.1).
2. The outcomes of any measurement of the observable associated with the operator  $\hat{A}$  are the eigenvalues  $a$  that satisfy the eigenvalue equation  $\hat{A}f = af$  (11.1.2).
3. The average value of the observable corresponding to  $\hat{A}$  is given by

$$\iiint_{-\infty}^{\infty} \psi^* \hat{A} \psi dV \quad (11.3.2)$$

where  $dV$  is the differential of volume in the coordinates used to express  $\psi$ . We can perform this operation in two dimensions (e.g. if a particle is confined to a plane) by replacing  $dV$  by  $dA$  and performing a double integral, or in one dimension, by performing a single integral and replacing  $dV$  by  $dx$ . In each case, we need to integrate over all space.

To illustrate these postulates let's consider the hydrogen atom again. The wavefunction for an electron in a 1s orbital is shown in Equation 11.3.1.

Quantum mechanical operators for some physical observables.

Observable	symbol in classical physics	Operator in QM	Operation
Position	$\mathbf{r}$	$\hat{\mathbf{r}}$	multiply by $\mathbf{r}$
Momentum	$p_x$	$\hat{p}_x$	$-i\hbar \frac{\partial}{\partial x}$
	$p_y$	$\hat{p}_y$	$-i\hbar \frac{\partial}{\partial y}$
	$p_z$	$\hat{p}_z$	$-i\hbar \frac{\partial}{\partial z}$
Kinetic Energy	$T$	$\hat{T}$	$-\frac{\hbar^2}{2m} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right)$
Potential Energy	$V(\mathbf{r})$	$\hat{V}(\mathbf{r})$	multiply by $\hat{V}(\mathbf{r})$
Total Energy	$E$	$\hat{H}$	$\hat{T} + \hat{V}$
Angular Momentum	$l_x$	$\hat{l}_x$	$-i\hbar \left( y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$

Observable	symbol in classical physics	Operator in QM	Operation
	$l_y$	$\hat{l}_y$	$-i\hbar(z\frac{\partial}{\partial x} - x\frac{\partial}{\partial z})$
	$l_z$	$\hat{l}_z$	$-i\hbar(x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x})$

Table 11.3.1: Quantum mechanical operators for some physical observables.

Let's say that we are able to measure the distance of the electron from the nucleus (i.e.  $r$ ). What will we measure? According to the postulates listed above, if the wavefunction of Equation 11.3.1 is an eigenfunction of the operator  $\hat{r}$ , then we will measure the corresponding eigenvalue. However, we can easily see that  $\hat{r}\psi \neq a\psi$ , since the operator  $r$  stands for "multiply by  $r$ ", and  $r \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-(r/a_0)} \neq a \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-(r/a_0)}$ . Remember that  $a$  should be a constant in Equation 11.3.1, so it cannot be a function of the coordinates  $(r, \theta, \phi)$ . The fact that  $\psi$  is not an eigenfunction of the operator  $\hat{r}$  means that a measurement of the position of the particle will give a value that we cannot predict. In other words, the position of the particle is not quantized, and we cannot know the result of the measurement with certainty. This should not be surprising to us, since we know that electrons do not move around the nucleus in fixed orbits as chemists once thought. Instead, we can talk about the probability of finding the electron at different values of  $r$ . A measurement of the observable  $r$  can in principle yield any value from 0 to  $\infty$ , although of course different values of  $r$  will be observed with different probabilities (see Section 10.4). Although we cannot predict the outcome of a single observation, we can calculate the average value of a very large number of observations (formally an infinite number of observations). We already calculated the average  $\langle r \rangle$  in Section 10.4. Let's do it again following the formalism of operators.

### ✓ Example 11.3.1

The wavefunction of the 1s orbital is expressed in polar coordinates as:

$$\psi(r, \theta, \phi) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-(r/a_0)}$$

Obtain  $\langle r \rangle$ .

#### Solution

For an observable  $A$ :

$$\langle A \rangle = \int_{all\ space} \psi^* \hat{A} \psi dV$$

For the observable  $r$ :

$$\langle r \rangle = \int_{all\ space} \psi^* \hat{r} \psi dV$$

where  $\hat{r}$  is the operator that corresponds to the observable  $r$ . According to Table 11.3.1, the operator  $r$  is "multiply by  $r$ ". Therefore:

$$\langle r \rangle = \int_{all\ space} \psi^* r \psi dV$$

For the 1s orbital,

$$\psi = \psi^* = \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0}$$

and then,

$$\langle r \rangle = \int_0^{2\pi} \int_0^\pi \int_0^\infty \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} r \frac{1}{\sqrt{\pi a_0^3}} e^{-r/a_0} r^2 \sin \theta \, dr \, d\theta \, d\psi$$

where  $\psi^*$  is shown in red,  $\hat{r}$  in black,  $\psi$  in blue, and  $dV$  in green.

We already solved this integral in Example 10.4.1, where we obtained

$$\langle r \rangle = \frac{1}{\pi a_0^3} \int_0^\infty e^{-2r/a_0} r^3 \, dr \int_0^{2\pi} d\psi \int_0^\pi \sin \theta \, d\theta = \frac{4}{a_0^3} \int_0^\infty e^{-2r/a_0} r^3 \, dr = \frac{3}{2} a_0$$

Therefore, the average value of  $r$  is  $3/2 a_0$ . Remember that  $a_0$  is a physical constant known as Bohr's radius, which is approximately  $0.53 \text{ \AA}$ , where  $1 \text{ \AA}$  (Angstrom) equals  $10^{-10} m$ .

**Important:** Because  $\hat{r}$  is "multiply by  $r$ ", and the wavefunction is real, the integrand becomes  $r\psi^2$ . However, you need to be careful when the operator involves derivatives. The integrand is the complex conjugate of the wavefunction multiplied by the function that you obtain when you calculate  $\hat{A}\psi$ . See Test Yourself 11.6 for an example where the order of the operations is important.

The result of Example 11.3.1 shows that the average distance of a 1s electron from the nucleus is  $3/2 a_0$ , which is about  $8 \times 10^{-10} m$ . The fact that the wavefunction is not an eigenfunction of the operator  $\hat{r}$  tells us that we cannot predict the result of a measurement of the variable  $r$ . What about other observables such as kinetic energy or total energy?

Are the orbitals of the hydrogen atom eigenfunctions of the operator  $\hat{T}$  (kinetic energy)? Let's try it with the 1s orbital of Equation 11.3.1 (our conclusion will be true for all other orbitals, as you will see in your advanced physical chemistry courses). Notice that the expressions of Table 11.3.1 are written in cartesian coordinates, while the orbitals are expressed in spherical coordinates. We could express the orbitals in cartesian coordinates, but that would be a lot of work because, in principle, there are infinite orbitals. It is much wiser to express the operators in spherical coordinates, so we can use them any time we need them in a problem that is best described in this coordinate system. This can be done using the chain rule, as we saw in previous chapters. In spherical coordinates, the operator  $\hat{T}$  is written as:

$$-\frac{\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) \quad (11.3.3)$$

where  $m$  is the mass of the particle (in this case the electron). If you compare this expression to the one found in Table 11.3.1 you may think we are complicating ourselves unnecessarily. However, it would be much more time consuming to convert every wavefunction we want to work with to cartesian coordinates, while obtaining Equation 11.3.3 from the expression in Table 11.3.1 is a one time job.

To see if the 1s orbital is an eigenfunction of the operator defined in Equation 11.3.3 we need to calculate

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

and see if the result equals a constant times the function  $\psi$ . The problem is solved in Example 11.3.2

### ✓ Example 11.3.2

Decide whether the 1s orbital

$$\psi(r, \theta, \psi) = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}} e^{-(r/a_0)}$$

is an eigenfunction of the operator  $\hat{T}$ , defined in Equation 11.3.3

#### Solution

The 1s orbital depends on  $r$  only, and therefore the derivatives with respect to  $\theta$  and  $\phi$  are zero (this will be true for all the s-orbitals). Therefore, Equation 11.3.3 reduces to:

$$\hat{T} = \frac{-\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) \right)$$

The function  $\psi$  is an eigenfunction of  $\hat{T}$  if the following relationship is true:

$$\hat{T}\psi = a\psi$$

Remember that  $a$  should be a constant (i.e. should not depend on  $r, \theta, \psi$ ).

Let's calculate  $\hat{T}\psi$ . We first need to calculate the derivative of  $\psi$  with respect to  $r$ , multiply the result by  $r^2$ , take the derivative with respect to  $r$  of the result, divide the result by  $r^2$ , and finally multiply the result by  $-\hbar^2/2m$ .

To simplify notation, let's call  $A = \frac{1}{\sqrt{\pi}} \frac{1}{a_0^{3/2}}$ , so that  $\psi(r, \theta, \psi) = Ae^{-(r/a_0)}$ .

$$\begin{aligned} \frac{\partial \psi}{\partial r} &= -\frac{A}{a_0} e^{-(r/a_0)} \\ \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) &= \frac{\partial}{\partial r} \left( r^2 \left( -\frac{A}{a_0} e^{-(r/a_0)} \right) \right) \\ &= -\frac{A}{a_0} \left( 2re^{-(r/a_0)} - \frac{1}{a_0} r^2 e^{-(r/a_0)} \right) \\ \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) &= -\frac{A}{a_0} \left( \frac{2}{r} e^{-(r/a_0)} - \frac{1}{a_0} e^{-(r/a_0)} \right) \\ \frac{-\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) &= \frac{A\hbar^2}{2ma_0} e^{-(r/a_0)} \left( \frac{2}{r} - \frac{1}{a_0} \right) \\ &= \frac{\hbar^2}{2ma_0} \left( \frac{2}{r} - \frac{1}{a_0} \right) \psi \neq a\psi \end{aligned}$$

Therefore,  $\psi$  is not an eigenfunction of  $\hat{T}$ , and we cannot predict the result of a measurement of the kinetic energy.

We will now consider the total energy (that is, the sum of the kinetic energy plus the potential energy). Because this is such an important property, the corresponding operator has a special name: the Hamiltonian ( $\hat{H}$ ). To write down the Hamiltonian, we need to add the kinetic energy operator (Equation 11.3.3) to the potential energy operator. However, in contrast to the kinetic energy term, the potential energy depends on the forces experienced by the particle, and therefore we cannot write a generic expression. If you took a physics course, you may be familiar with different expressions for the potential energy of different systems (e.g. two charged particles, a spring, a particle in a gravitational field, etc). In all cases, the potential energy depends on the coordinates of the particles. For example, for two charged point particles of opposite sign, the electrostatic potential associated with their interaction is  $V(r) = kq_1q_2/r$ . Here,  $k$  is a constant (see below),  $q_1$  and  $q_2$  are the charges of the two particles, and  $r$  is the distance that separates them. If you look at table [tab:operators], you will see that the operator that corresponds to this expression is just “multiply by...”. This is because the potential energy depends on the coordinates, and not on the derivatives. Therefore, it is like the operator  $\hat{r}$  we saw before. For the hydrogen atom, the potential energy arises from the interaction between the only electron and the only proton in the atom. Both have the same charge (in absolute value), but one is negative and the other one positive, so  $q_1q_2 = -\epsilon^2$ , where  $\epsilon$  is the charge of the proton. With this in mind, we can write the operator  $\hat{V}$  as:

$$\hat{V} = -\frac{\epsilon^2}{4\pi\epsilon_0} \frac{1}{r}$$

It is important to understand that this is an operator which operates by “multiplying by...”. Therefore  $\hat{V}\psi = -\frac{\epsilon^2}{4\pi\epsilon_0} \frac{1}{r} \psi$ . A common mistake is to forget the wavefunction  $\psi$ . The Hamiltonian for the hydrogen atom can then be expressed as the sum  $\hat{T} + \hat{V}$ :

$$\hat{H} = \frac{-\hbar^2}{2m} \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left( \sin \theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) - \frac{\epsilon^2}{4\pi\epsilon_0} \frac{1}{r} \quad (11.3.4)$$

According to the postulates of quantum mechanics, if the wavefunction defined in Equation 11.3.1 is an eigenfunction of this Hamiltonian, every time we measure the total energy of the electron we will measure the corresponding eigenvalue. In other words, if this is true:  $\hat{H}\psi = a\psi$ , then the constant  $a$  is the energy of one electron in the 1s orbital. If we used the wavefunction for the 2s orbital instead, we would get the energy of the 2s orbital, and so on. It is important to note that the constants in the potential energy term are related to Bohr radius ( $a_0$ ) as:

$$\frac{e^2}{4\pi\epsilon_0} = \frac{\hbar^2}{ma_0}.$$

This relationship will allow you to simplify your result.

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