

7.10: Operators, Eigenfunctions and Eigenvalues

Sooner or later any books on quantum mechanics will bring in these words. There will also be discussions about whether certain pairs of operators do or do not commute. What is this all about?

Recall that Schrödinger's Equation is equation 7.8.5, and, for hydrogenlike atoms we use the Equation 7.9.1 for the potential energy. We might like to solve Equation 7.8.5 to find the wavefunctions. In fact mathematically-minded people have already done that for us, and I have reproduced the result as Equation 7.9.5. We might well also be interested to know the value of the total energy E for a given eigenfunction. Equation 7.8.5 can be rearranged to read:

$$\left(V - \frac{\hbar^2}{2m} \nabla^2\right) \psi = E\psi. \quad (7.10.1)$$

This tells us that, if we operate on the wavefunction with the expression in parentheses, the result of the operation is that you end up merely with the same function, multiplied by E . Seen thus, we have an *eigenvalue problem*. The solution of the Schrödinger equation is tantamount to seeking a function that is an eigenfunction of the operator in parentheses. The operator in parentheses, for reasons that are as obvious to me as they doubtless would have been to the nineteenth century Scottish-Irish mathematician Sir William Hamilton, is called the *hamiltonian operator* H . Thus Equation 7.10.1 can be written as

$$H\psi = E\psi. \quad (7.10.2)$$

If we choose, instead of writing out the wavefunction in full, merely to list its quantum number inside a ket, Schrödinger's equation, written in operator-ket form becomes

$$H|lmn\rangle = E|lmn\rangle. \quad (7.10.3)$$

And what do we get for the eigenvalue of the hamiltonian operator operating on the hydrogenlike eigenfunction? We'll leave it to the mathematically inclined to work through the algebraic details, but what we get is the very same expression, Equation 7.4.7, that we got for the energy levels in Section 7.4 when we were dealing with the Bohr model - but this time without the arbitrary Bohr assumptions. This is exciting stuff! (Before we get too carried away, however, we'll note that, like the original Bohr model with circular orbits, this model predicts that the energy levels depend solely upon the one quantum number n . Fine structure of the lines, however, visible only with difficulty in hydrogenlike atoms, but much more obvious in more complex spectra, suggests that this isn't quite good enough yet. But we still don't deny that it is exciting so far.)

I hope this may have taken some of the mystery out of it - though there is a little more to come.

I used to love attending graduate oral examinations. After the candidate had presented his research with great confidence, one of my favorite questions would be: "What is the significance of pairs of operators that commute?" In case you ever find yourself in the same predicament, I shall try to explain here. Everyone knows what commuting operators are. If two operators A and B commute, then it doesn't matter in which order they are performed - you get the same result either way. That is, $AB\psi = BA\psi$. That is, the *commutator* of the two operators, $AB - BA$, or, as it is often written, $[A, B]$, is zero. So much anyone knows. But that is not the question. The question is: What is the *significance* of two operators that commute? Why are commuting pairs of operators of special interest? The significance is as follows:

If two operators commute, then there exists a function that is simultaneously an eigenfunction of each; conversely if a function is simultaneously an eigenfunction of two operators, then these two operators necessarily commute.

This is so easy to see that it is almost a truism. For example, let ψ be a function that is simultaneously an eigenfunction of two operators A and B , so that $A\psi = a\psi$ and $B\psi = b\psi$. Then

$$AB\psi = Ab\psi = bA\psi = ba\psi = ab\psi \quad (7.10.1)$$

and

$$BA\psi = Ba\psi = aB\psi = ab\psi. \quad (\text{Q.E.D.})$$

It therefore immediately becomes of interest to know whether there are any operators that commute with the hamiltonian operator, because then the wavefunction 7.9.5 will be an eigenfunction of these operators, too, and we'll want to know the corresponding eigenvalues. And any operators that commute with the hamiltonian operator will also commute with each other, and all will have

equation 7.9.5 as an eigenfunction. (I interject the remark here that the word "hamiltonian" is an adjective, and like similar adjectives named after scientists, such as "newtonian", "gaussian", etc., is best written with a small initial letter. Some speakers also treat the word as if it were a noun, talking about "the hamiltonian". This is an illiteracy similar to talking about "a spiral" or "an elliptical" or "a binary", or, as is heard in bird-watching circles, "an Orange-crowned". I hope the reader will not perpetuate such a degradation of the English language, and will always refer to "the hamiltonian operator".)

Let us return briefly to the wavefunction that describes a moving particle discussed at the end of section 7.8, and specifically to the time-dependent equation 7.8.9. The total energy of such a particle is the sum of its kinetic and potential energies, which, in nonrelativistic terms, is given by

$$E = \frac{p^2}{2m} + V. \quad (7.10.4)$$

If we compare this with equation 7.8.9 we see that we can write this in operator form if we replace E by the operator $i\hbar \frac{\partial}{\partial t}$ and \mathbf{p} by the operator $-i\hbar \nabla$ (or, in one dimension, p_x by $-i\hbar \frac{\partial}{\partial x}$).

(The minus sign for p is chosen to ensure that ψ is a periodic rather than an exponentially expanding function of x .)

Now let us return to the hydrogen atom and ask ourselves what is the orbital angular momentum \mathbf{l} of the electron. The angular momentum of a particle with respect to an origin (i.e. the nucleus) is defined by $\mathbf{l} = \mathbf{r} \times \mathbf{p}$, where \mathbf{p} is the linear momentum and \mathbf{r} is the position vector with respect to the origin. In rectangular coordinates it is easy to write down the components of this vector product:

$$l_x = yp_z - zp_y, \quad (7.10.5)$$

$$l_y = zp_x - xp_z, \quad (7.10.6)$$

$$l_z = xp_y - yp_x. \quad (7.10.7)$$

Writing these equations in operator form, we have:

$$l_x \equiv -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right) \quad (7.10.8)$$

and similar expressions for the operators \mathbf{l}_y and \mathbf{l}_z . Do any two of these commute? Try \mathbf{l}_x and \mathbf{l}_y . You'll find very soon that they do not commute, and in fact you should get

$$[l_x, l_y] \equiv i\hbar l_z \quad (7.10.9)$$

and two similar relations obtained by cyclic permutation of the subscripts. Indeed in the context of quantum mechanics any operator satisfying a relation like 7.10.9 is defined as being an angular momentum operator.

We have been using spherical coordinates to study the hydrogen atom, so the next thing we shall want to do will be to express the operators \mathbf{l}_x , \mathbf{l}_y and \mathbf{l}_z in spherical coordinates. This will take a little time, but if you do this, you will obtain two rather complicated expressions for the first two, but the third one turns out to be very simple:

$$l_z \equiv -i\hbar \frac{\partial}{\partial \phi}. \quad (7.10.10)$$

Now look at the wavefunction 7.9.5. Is this by any chance an eigenfunction for the operator 7.10.10? By golly – it is, too! Just carry out that simple operation, and you will immediately find that

$$l_z |lmn\rangle = m |lmn\rangle. \quad (7.10.11)$$

In writing this equation, we are expressing angular momentum in units of \hbar . Since $|lmn\rangle$ is an eigenfunction of the hamiltonian operator as well as of the z -component of the angular momentum operator, \mathbf{l}_z and H must commute.

We have just found that the function $|lmn\rangle$ is an eigenfunction of the operator \mathbf{l}_z and that the operator has the eigenvalue m , a number that, for a given l can have any of the $2l + 1$ integral values from $-l$ to $+l$.

If you are still holding on to the idea of a hydrogen atom being a proton surrounded by an electron moving in circular or elliptical orbits around it, you will conclude that the only orbits possible are those that are oriented in such a manner that the z -component of the angular momentum must be an integral number of times \hbar , and you will be entirely mystified by this magical picture. Seen

from the point of view of wave mechanics, however, there is nothing at all mysterious about it, and indeed it is precisely what one would expect. All we are saying is that the distribution of electrons around the nucleus is described by a probability amplitude function that must have an integral number of antinodes in the interval $\phi = 0$ to 2π , in exactly the same way that we describe the vibrations of a sphere. It is all very natural and just to be expected.

I shall not go further into the algebra, which you can either do yourself (it is very straightforward) or refer to books on quantum mechanics, but if you write out in full the operator L^2 (and you can work in either rectangular or spherical coordinates) you will soon find that it commutes with L_z and hence also with H , and hence $|lmn\rangle$ is an eigenfunction of it, too. The corresponding eigenvalue takes a bit more algebra, but the result, after a bit of work, is

$$L^2|lmn\rangle = l(l+1)|lmn\rangle. \quad (7.10.12)$$

As before, we are expressing angular momentum in units of \hbar .

There is much, much more of this fascinating stuff, but I'll just pause here to summarize the results.

The energy levels are given by equation 7.4.7, just as predicted from the Bohr model. They involve only the one quantum number (often called the "principal" quantum number) n , which can have any nonnegative integral value. Orbital angular momentum can take the values $\sqrt{l(l+1)}\hbar$, where, for a given n , l can have the n integral values from 0 to $n-1$. The z -component of angular momentum can have, for a given value of l , the $2l+1$ integral values from $-l$ to $+l$. For a given value of n there is a total of n^2 possible combinations of l and m .

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