CHM 305 - Lecture 5 - Quantum Operators and Eigenfunctions

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We are now going to work towards the big rules of the game, which are usually referred to as the "Postulates of Quantum Mechanics." This lecture will develop some useful tools, which we will then use to explore the Postulates in the two following lectures. This material is covered in Chapter 4 of McQuarrie.

1 Quantum Operators

In quantum mechanics, **every measurable physical quantity (e.g. energy, momentum, position) is called an *observable***. Each observable has a corresponding operator, which we denote with a caret like $\hat{O}$. Operators simply tell you to "do something" to whatever follows them. We already know some examples of operators:

- $\hat{H} = \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$, the Hamiltonian, or energy operator, in one dimension
- $\hat{x} = x$, the position operator is simply multiplication by x
- $\hat{p} = -i\hbar\frac{\partial}{\partial x}$, the momentum operator, closely related to differentiation by x. (See the note at the end of this document for more on where this definition of $\hat{p}$ comes from.)

1.1 Quantum operators have eigenfunctions and eigenvalues

When we solve the time-independent Schrödinger equation

$$\hat{H}\psi_n(x) = E_n\psi_n(x) \tag{1}$$

we are actually solving an *eigenvalue problem* where the eigenfunctions ψ_n are a set of special functions that when acted on by that operator return themselves times a number. And the special number E_n is the eigenvalue that corresponds to the n^{th} eigenfunction. If you are familiar with linear algebra, a useful analogy is that operators can be represented by matrices with eigenfunctions represented by vectors. *Note: There is an entire formalism of quantum mechanics based around matrices, which we will only touch on in this course. If you take graduate level quantum mechanics you will see a lot more of that.*

In quantum mechanics, **eigenvalues are always real and represent measurable values of the observable**. Using the Hamiltonian operator as an example, our observable is energy and the eigenvalue E_n represents the energy of the system when it is in the $\psi_n(x)$ eigenstate (or stationary state).

Practice Problem 1: Check if $\psi(x) = \sin(kx)$ is an eigenfunction of the following operators:

$$\hat{A} = \frac{d}{dx} \tag{2}$$

$$\hat{B} = \frac{d^2}{dx^2} \tag{3}$$

If you find $\psi(x)$ to be an eigenfunction of one of these operators, what is its eigenvalue?

1.2 Quantum operators are linear

If $\hat{A}$ is an operator with eigenfunctions ψ_1 and ψ_2 and corresponding eigenvalues a_1 and a_2, then:

$$\hat{A}(c_1\psi_1 + c_2\psi_2) = c_1 a_1 \psi_1 + c_2 a_2 \psi_2 \tag{4}$$

assuming c_1 and c_2 are constants. In other words, $\hat{A}$ acts independently on each function in turn.

To further generalize this phenomenon, if $\{\psi_n\}$ are the set of eigenfunctions of $\hat{A}$ with corresponding eigenvalues $\{a_n\}$ then:

$$\hat{A}\sum_{i=1}^{\infty} c_i\psi_i = \sum_{i=1}^{\infty} c_i a_i \psi_i \tag{5}$$

1.3 Quantum operators need not commute

It's important to act with operators in the correct order, just as is true for matrix multiplication. Whichever operator is nearest to the wavefunction always acts first:

$$\hat{A}\hat{B}\psi(x) = \hat{A}\Big(\hat{B}\psi(x)\Big) \tag{6}$$

Another way to say this is that operators do not necessarily commute, so in general:

$$\hat{A}\hat{B}\psi(x) \neq \hat{B}\hat{A}\psi(x) \tag{7}$$

In fact, in the rare cases where two operators *do* commute with one another, it implies that they have a very special relationship, which we will learn more about later.

We will also use something called a *commutator* as shorthand:

$$\Big[\hat{A}, \hat{B}\Big]\,\psi \equiv (\hat{A}\hat{B} - \hat{B}\hat{A})\psi \tag{8}$$

where $[\hat{A}, \hat{B}] = 0$ if the operators commute and $[\hat{A}, \hat{B}] \neq 0$ if they do not.

Practice Problem 2: Do the operators $\hat{A} = \frac{d}{dx}$ and $\hat{B} = x$ commute? *Hint: evaluate* $[\hat{A}, \hat{B}]\psi$.

2 Eigenfunctions of Quantum Operators

Let's hammer out a few rules for how eigenfunctions of quantum mechanical operators should behave. Eigenfunctions have some peculiar properties that we'll need to make use of as we proceed.

Consider again the set of eigenfunctions of the operator $\hat{A}$, which we will call $\{\psi_n(x)\}$. By definition, the eigenfunctions have the property that when operated on by $\hat{A}$, they return themselves times a constant, their eigenvalue:

$$\hat{A}\psi_n(x) = a_n\psi_n(x) \tag{9}$$

2.1 Eigenfunctions are normalized

For each eigenfunction $\psi_n(x)$ we will mandate that the integral of the eigenfunction's magnitude over all space be normalized to 1:

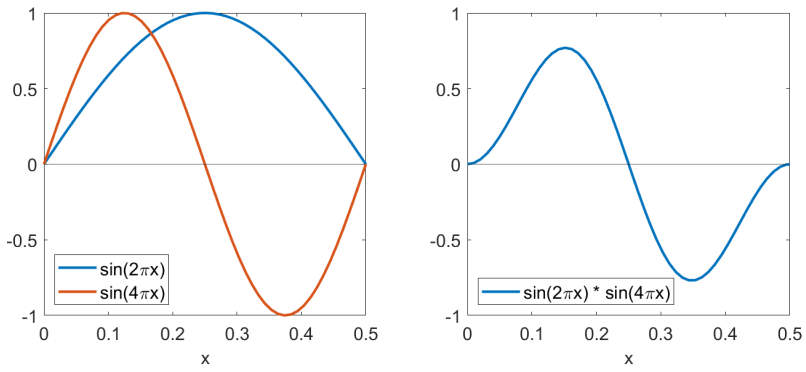
$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_n(x)dx = \int_{-\infty}^{\infty} |\psi_n(x)|^2 dx = 1 \tag{10}$$

Note: $\psi_n^*(x)$ is the complex conjugate of $\psi_n(x)$. If $\psi_n(x)$ is real, then $\psi_n(x) = \psi_n^*(x)$. Why do we need to take the complex conjugate? $\psi_n(x)$ may be complex, and the magnitude of a complex number $y = a + ib$ is given by $|y|^2 = y^* \cdot y = (a - ib) \cdot (a + ib)$.

Normalization is important because wavefunctions represent probability distributions for where we expect to find a particle. We want the total probability that the particle be found *somewhere* in space to be 1.

Practice Problem 3: Normalize the wavefunction $\psi(x) = c \cdot (1 - x)$ over the interval $[0, 1]$. *Hint:* Solve for c assuming that $\int_0^1 |\psi(x)|^2 dx = 1$.

2.2 Eigenfunctions of the same operator are orthogonal



Consider again our infinite set of functions $\psi_n(x)$, which are all eigenfunctions of the same operator $\hat{A}$. It turns out that any pair of eigenfunctions with $m \neq n$ are orthogonal. Two functions are by definition orthogonal if:

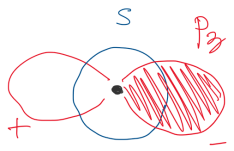
$$\int_{-\infty}^{\infty} \psi_n^*(x)\psi_m(x)dx = 0 \tag{11}$$

What this means physically is that each eigenfunction must be independent of the others - they do not interfere or overlap. As an example, the set of functions

$$\psi_n(x) = \sin(2\pi n x) \quad n = 1, 2, 3, \ldots \tag{12}$$

are all mutually orthogonal. Above, we plot the first two of these functions over the interval $x = [0, 1/2]$. You should be able to convince yourself that the net overlap of these two functions is exactly 0 over the interval shown. In particular, if you consider the product of these two functions as plotted in the righthand panel above, by inspection we can see that the integral of this quantity will vanish over one complete oscillation.

Another good example of orthogonal functions are atomic orbitals. Visualize an atomic s orbital and a p orbital. Because the p orbital has two nodes with amplitudes of opposite sign, its net overlap with the s orbital over all space is 0. Any pair of atomic orbitals you might choose are similarly orthogonal over all (3D) space.



2.3 Eigenfunctions of the same operator are *orthonormal*

Putting together our results from the past two points, we can make a more general statement that the set of eigenfunctions $\{\psi_n(x)\}$ of the same operator is *orthonormal*, meaning each eigenfunction is normalized, and each pair of distinct eigenfunctions is orthogonal.

We can summarize this result as:

$$\int_{-\infty}^{\infty} \psi_m^*(x)\psi_n(x)dx = \delta_{mn} = \begin{cases} 0, & m \neq n \\ 1, & m = n \end{cases} \tag{13}$$

where δ_{mn} is a useful shorthand called the "Kronecker delta."

Practice Problem 4: Show that the set of functions $\psi_n(x) = \frac{1}{\sqrt{2\pi}} e^{inx}$ is orthonormal over the window $-\pi \leq x \leq \pi$ provided that n is an integer. To do so, you will need to show that the integral

$$\int_{-\pi}^{\pi} \psi_m^*(x)\psi_n(x)dx = \begin{cases} 1 & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases}$$

2.4 Eigenfunctions of the same operator form a complete set

We will often construct wavefunctions out of linear combinations of "basis functions." To give a familiar example, we build molecular orbitals as linear combinations of atomic orbitals.

If our basis functions $\{\psi_n(x)\}$ are the infinite ladder of eigenfunctions for a quantum mechanical operator $\hat{A}$, then they form a *complete basis set.* This means that for *any* arbitrary wavefunction

$\rho(x)$, we can find coefficients b_n such that:

$$\rho(x) = \sum_{n=1}^{\infty} b_n \psi_n(x) = b_1\psi_1(x) + b_2\psi_2(x) + \cdots + b_m\psi_m(x) + \ldots \tag{14}$$

How do we go about finding the correct set of coefficients $b_1, b_2, \ldots b_m, \ldots$ to represent the desired $\rho(x)$? We can actually derive an expression for any given coefficient very simply, using the orthogonality relation we just discussed for eigenfunctions.

Consider the following integral, which we can think of as an *overlap* integral between $\rho(x)$ and one of the eigenfunctions. Let's evaluate this for $\psi_2(x)$ as a concrete example:

$$\int_{-\infty}^{+\infty} \psi_2^*(x)\rho(x)dx \tag{15}$$

$$= \int_{-\infty}^{+\infty} \psi_2^*(x) \left[\sum_{n=1}^{\infty} b_n\psi_n(x)\right] dx \tag{16}$$

$$= \sum_{n=1}^{\infty} b_n \int_{-\infty}^{+\infty} \psi_2^*(x)\psi_n(x)dx \tag{17}$$

$$= \sum_{n=1}^{\infty} b_n\delta_{2n} = b_2 \quad \checkmark \tag{18}$$

In the last step, we used the fact that the basis is orthonormal, so only the term in the sum where $n = 2$ survives, since

$$\delta_{2n} = \begin{cases} 0, & n \neq 2 \\ 1, & n = 2 \end{cases} \tag{19}$$

More generally, for the n^{th} coefficient in the sum, we have

$$b_n = \int_{-\infty}^{+\infty} \psi_n^*(x)\rho(x)dx \tag{20}$$

So it proves to be quite straightforward to find the set of b_n coefficients and express $\rho(x)$ as an expansion of eigenfunctions:

$$\rho(x) = \sum_{n=1}^{\infty} b_n\psi_n(x) = \sum_{n=1}^{\infty} \left[\int_{-\infty}^{+\infty} \psi_n^*(x)\rho(x)dx\right] \psi_n(x) \tag{21}$$

This is a very important and useful property of eigenfunctions. This is a concept closely related to Fourier series, if you have seen that in previous coursework.

Practice Problem 5: Let's again work with the set of orthonormal basis functions

$$\psi_n(x) = \frac{1}{\sqrt{2\pi}} e^{inx}, \quad n = 1, 2, \ldots$$

defined over the window $-\pi \leq x \leq \pi$.

Say I prepare a wavefunction in a specific linear combination of these basis functions, given by:

$$\begin{aligned} \rho(x) &= \frac{1}{\sqrt{2}}\psi_1(x) + \frac{1}{\sqrt{2}}\psi_2(x) \\ &= \sum_{n=1}^{\infty} b_n \psi_n(x) \qquad \text{with} \quad b_1 = b_2 = \frac{1}{\sqrt{2}}, \quad b_{n>2} = 0 \end{aligned}$$

Confirm that

$$b_1 = \int_{-\pi}^{\pi} \psi_1^*(x)\rho(x)dx$$

3 An aside on the momentum operator

Another quick note, which will become relevant later, but is worth drawing your attention to now: if we consider the kinetic energy term of the Hamiltonian, and connect it to what we know about kinetic energy, we find

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2} = \frac{p^2}{2m} \tag{22}$$

$$\rightarrow \hat{p} = -i\hbar\frac{\partial}{\partial x} \tag{23}$$

where $\hat{p}$ is the *momentum operator*!

Another way to derive the momentum operator is to consider a free quantum particle wavefunction

$$\psi(x,t) = e^{i(px-Et)/\hbar} \tag{24}$$

and consider

$$\frac{\partial\psi}{\partial x} = \frac{\partial}{\partial x}\left[e^{i(px-Et)/\hbar}\right] \tag{25}$$

$$= \frac{ip}{\hbar}e^{i(px-Et)/\hbar} = \frac{ip}{\hbar}\psi(x,t) \tag{26}$$

Rearranging, we find:

$$p\psi(x,t) \equiv \hat{p}\psi(x,t) = \frac{\partial\psi}{\partial x}\cdot\hbar\cdot\frac{1}{i} = -i\hbar\frac{\partial}{\partial x}\left[\psi\right] \tag{27}$$

$$\rightarrow \quad \boxed{\hat{p} = -i\hbar\frac{\partial}{\partial x}} \tag{28}$$