Crash Course on Quantum Mechanics, Part II

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Abstract

In order to understand the underlying principles of quantum mechanics we will present the formalism of how a Hilbert space functions and what rules it imposes on the structure of a wavefunction. As examples we will explore the cases of the infinite-square well and the quantum harmonic oscillator.

1. Expected Value

Typically whenever talking about quantum mechanics it is quite convenient to introduce *bra-ket notation* as was introduced by Paul Dirac. To make this formal we first mention that the space of states for a quantum mechanical system is modeled by a *Hilbert space*.

Definition 1.1 (Hilbert Space)**.** A Hilbert space $\mathscr{H}$ is a complex inner product space that is a complete metric space.

In case some of the terms above are not familiar we mention the details now. A complex inner product is a function:

$$\langle \cdot, \cdot \rangle : \mathbb{C} \times \mathbb{C} \to \mathbb{R}$$

that for vectors $x, y \in \mathscr{H}$ and constants $a, b \in \mathbb{C}$ satisfies:

- Symmetric Conjugation: $\langle x, y \rangle = \langle y, x \rangle^*$
- Linearity in First Component: $\langle ax_1 + bx_2, y \rangle = a\langle x_1, y \rangle + b\langle x_2, y \rangle$
- Positive-Definite: $\langle x, x \rangle \geq 0$ with equality if and only if $x = 0$

With an inner product we can form the magnitude of a vector x via $|x| = \sqrt{\langle x, x \rangle}$ and formulate the distance between two vectors x and y through $d(x, y) = |x - y| = \sqrt{\langle x - y, x - y \rangle}$. Given all of this structure it becomes natural to think of a Hilbert space as a metric space on which Cauchy sequences can be discussed and consequently the term *complete* in the definition references to the fact that all Cauchy sequences are convergent. Equivalently, we can think of this property as stating that for a collection of vectors $\{v_n\}_{n=1}^{\infty}$ in $\mathscr{H}$:

$$\sum_{n=1}^{\infty} v_n \text{ converges in } \mathscr{H} \quad \Longleftrightarrow \quad \sum_{n=1}^{\infty} |v_n| < \infty$$

With all of the above in mind we can now formulate how a Hilbert space fits as the model for quantum mechanics. Letting:

$$\langle \Psi | = \int_{-\infty}^{\infty} \mathrm{d}x \ \Psi^*$$

we take the convention that:

$$\langle \Psi \mid \Psi \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \ \Psi^* \Psi$$

Thus, for a *ket* $|\Psi\rangle$ representing the wavefunction of a particle we can pair it to a *bra* $\langle \Psi|$ so as to produce some sort of measurement. More generally, the notation above is used to define the *expected* value of an operator A via:

$$\langle A \rangle = \langle \Psi \mid A \mid \Psi \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \ \Psi^* A \Psi$$

As far as operators go there are a great many to focus on, but for now we choose to focus on the *position* and *momentum* operators, denoted by x and p, respectively. For the case of position we simply have:

$$\langle x \rangle = \langle \Psi \mid x \mid \Psi \rangle = \int_{-\infty}^{\infty} \mathrm{d}x \ \Psi^* x \Psi$$

Building off of this we now take the derivative and observe what happens:

$$\begin{aligned}\frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^* x\Psi \\ &= \int_{-\infty}^{\infty}\mathrm{d}x\left(\frac{\partial\Psi^*}{\partial t}\Psi + \Psi^*\frac{\partial\Psi}{\partial t}\right)x \\ &= \frac{i\hbar}{2m}\int_{-\infty}^{\infty}\mathrm{d}x\ x\frac{\partial}{\partial x}\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right) \\ &= -\frac{i\hbar}{2m}\int_{-\infty}^{\infty}\mathrm{d}x\left(\Psi^*\frac{\partial\Psi}{\partial x} - \frac{\partial\Psi^*}{\partial x}\Psi\right) \\ &= -\frac{i\hbar}{m}\int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^*\frac{\partial\Psi}{\partial x}\end{aligned}$$

where we used the Schrödinger equation (and its conjugate version) from the second to third line and integration by parts for the fourth and fifth lines. Now we identify:

$$\langle v\rangle = -\frac{i\hbar}{m}\int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^*\frac{\partial\Psi}{\partial x}$$

where v is the velocity of the particle. Using the classical formulation that $p = mv$ we deduce that the expected value of the momentum operator is given by:

$$\langle p\rangle = -i\hbar\int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^*\frac{\partial\Psi}{\partial x} = \int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\Psi$$

With the expression on the right-hand side we can now formally identify the momentum operator as:

$$p = -i\hbar\frac{\partial}{\partial x}$$

which is a hard definition to understand intuitively since it is defined in terms of a derivative operator, not the derivative of some function. Now recall that in the classical context the *kinetic energy* of the particle is defined as $T = \frac{p^2}{2m}$, which allows us to compute its expected value in the quantum mechanical world:

$$\langle T\rangle = \int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^*\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\right)\Psi = -\frac{\hbar^2}{2m}\int_{-\infty}^{\infty}\mathrm{d}x\ \Psi^*\frac{\partial^2\Psi}{\partial x^2}$$

2. Infinite-Square Well

Now let us turn our attention towards a very specific scenario known as the *infinite-square well*. In this particular case we are given the potential:

$$V(x) = \begin{cases} 0, & x \in [0,a] \\ \infty, & x \notin [0,a]\end{cases}$$

where in essence this potential guarantees that our particle exists strictly inside the domain $[0,a]$ and cannot possibly escape it. The time-independent Schrödinger equation inside the domain reduces down to:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi$$

where by setting $k = \frac{\sqrt{2mE}}{\hbar}$ the above can be rewritten in the form:

$$\psi'' + k^2\psi = 0$$

For this second-order constant-coefficient linear differential equation the general solution will be given by:

$$\psi(x) = A\sin(kx) + B\cos(kx)$$

where A and B are coefficients that have to be determined from initial/boundary conditions and for this solution we take $\psi(0) = \psi(a) = 0$ in order to guarantee the continuity of the wavefunction at the boundaries. By plugging in we find that $\psi(0) = 0$ forces $B = 0$ and for $\psi(a) = 0$ we must have:

$$0 = A\sin(ka)$$

Now if $A = 0$ then we are left with the trivial solution which is not the one we desire. Thus, to avoid this from occurring we must have $\sin(ka) = 0$, or equivalently $ka = n\pi$ for $n \in \mathbb{Z}$. With this in mind we introduce the notation $k_n = \frac{n\pi}{a}$ to express the explicit dependence on n and revisiting the previous substitution we arrive at:

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2}$$

Thus, this shows that the particle at play will have quantized energy levels with each value associated to some natural number. Most interestingly notice that the ground-state energy is given by the value $E_1 = \frac{\pi^2\hbar^2}{2ma^2}$ which contrasts greatly with the result predicted from classical mechanics that says the ground state energy should be zero. We will come back to this aspect later to show how it relates to the *uncertainty principle*.

Notice by this point that while we have avoided setting $A = 0$ we have yet to determine a value for it. In order to pull this off we recall that we have a normalization constraint, namely:

$$1 = \int_0^a |A|^2 \sin^2(k_n x)\, \mathrm{d}x = |A|^2 \cdot \frac{a}{2}$$

Isolating the coefficient in the work above we find that $A = \sqrt{\frac{2}{a}}$ providing us with the final solution:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi}{a}x\right)$$

Since the differential equation was linear to begin with we form the general solution by taking the linear combination of all possibilities:

$$\psi(x) = \sum_{n=1}^{\infty} c_n\psi_n(x) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right) \quad \text{and} \quad \Psi(x,t) = \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty} c_n \sin\left(\frac{n\pi}{a}x\right)e^{-\frac{iE_n t}{\hbar}}$$

It can be checked rigorously that the collection $\{\psi_n(x)\}_{n=1}^{\infty}$ form an orthonormal basis through the inner product:

$$\langle \psi_m \mid \psi_n \rangle = \int_{-\infty}^{\infty} \mathrm{d}x\ \psi_m^* \psi_n = \delta_{mn}$$

Furthermore, it can also be checked that ψ_n as a function is either even or odd depending on the value of n. More specifically, the even/odd behavior alternates between successive values of n.