

# Wave Mechanics

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April 2015

## 1 Introduction

*“There is nothing new to be discovered in physics now, All that remains is more and more precise measurement.”* ~ Lord Kelvin, 1900

After the discovery of electrodynamics and its Lorentz invariance, physics at the beginning of the 20<sup>th</sup> century appeared to be coming together into a complete picture under the pillars of mechanics and electromagnetism. However, a few anomalous effects proved to be incongruous with classical theory, and Kelvin’s picture of a complete physics was toppled. The quantum theory managed to resolve the difficulties presented by these anomalies. The theory was developed from multiple different angles. One approach, now called the old quantum theory, quantized the ideas of Hamiltonian mechanics; this was sufficient for describing the quantum harmonic oscillator. However, it turns out that the old quantum theory is the second term in an expansion that begins with classical mechanics; it is still only an approximation to the truth. The full-fledged quantum theory was developed by Schrödinger and Heisenberg in two very different-seeming forms which are in fact equivalent. Today we will look at Schrödinger’s formulation, also known as wave mechanics.

## 2 The Schrödinger Equation

The anomalous effects that led to the development of quantum theory were all concerned with waves acting like particles and particles acting like waves. In order to describe this behavior, we need some theory that unifies waves and particles. We don’t have any way of describing waves in terms of particles; however, we do know how to decompose particle motion into wave motion using the Fourier transform. This suggests that waves are more fundamental; we can attempt to determine a wave theory for mechanics.

We have studied the wave equation in previous lectures.

$$\nabla^2 \Psi = \frac{1}{c^2} \frac{\partial^2 \Psi}{\partial t^2}$$

We know that its solutions take the form

$$\Psi(\mathbf{r}, t) = Ae^{i(k\mathbf{r} - \omega t)}.$$

Now we can begin mixing this waveform with particle-related quantities. We know from the photoelectric effect that  $E = hf = \hbar\omega$ . We also know the de Broglie wavelength of a particle is

$$\lambda = \frac{h}{mv},$$

so  $p = \hbar k$ . We can thus rewrite the wavefunction as

$$\Psi(\mathbf{r}, t) = Ae^{\frac{i}{\hbar}(p\mathbf{r} - Et)}.$$

Therefore,

$$\nabla \Psi = \frac{i}{\hbar} p \Psi,$$

so that we can formally write

$$p = -i\hbar \nabla.$$

Similarly,

$$E = i\hbar \frac{\partial}{\partial t}.$$

However, we also know that  $E = \frac{p^2}{2m} + V(\mathbf{r})$ . So, we can write

$$i\hbar \frac{\partial}{\partial t} = -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}).$$

This identity is given significance when we allow each side to operate on an actual wavefunction  $\Psi$ . With some minor rearrangements, this gives the Schrödinger equation.

$$\left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}$$

This is a partial differential equation which happens to be separable. If we substitute  $\Psi(\mathbf{r}, t) = \psi(\mathbf{r})\phi(t)$ , the equation becomes

$$\frac{1}{\psi} \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right] \psi = i\hbar \frac{1}{\phi} \frac{\partial \phi}{\partial t}.$$

Note that we have rearranged the equation so that the left side depends only on  $\mathbf{r}$  and the right side only on  $t$ . This means that each side must be equal to a constant, which we call  $E$ .

$$\begin{aligned} \left[ -\frac{\hbar^2 \nabla^2}{2m} + V(\mathbf{r}) \right] \psi &= E\psi \\ i\hbar \frac{\partial \phi}{\partial t} &= E\phi \end{aligned}$$

We can immediately solve the second equation to give

$$\phi = e^{-\frac{i}{\hbar} Et}.$$

The first equation is the time-independent Schrödinger equation; it says that the energy  $E$  must be equal to one of the eigenvalues of the operator on the left. This operator is known as the Hamiltonian  $\hat{H}$ , and so we often write the time-independent Schrödinger equation compactly as

$$\hat{H}\psi = E\psi.$$

### 3 Wavefunctions

Now that we have derived the fundamental equations governing the wavefunction  $\psi$ , we need to know what this wavefunction actually represents. The Born rule states that  $|\psi(x, y, z, t)|^2 dV$  gives the probability of finding a particle in the volume element  $dV$  at time  $t$ . This means that the magnitude squared of a wavefunction must be a valid probability distribution; i.e., it is normalized.

$$\int \psi^* \psi d\tau = 1$$

Note that  $d\tau$  signifies an integral extending over the entire configuration space.

To illustrate the physical significance of the wavefunction, we can consider a simple example of a one-dimensional Gaussian wavepacket.

$$\psi(x, 0) = Ae^{-\frac{x^2}{2d^2}}$$

Note that the form of this wavefunction depends only on  $d$ ; once we fix  $d$ ,  $A$  is fixed by the normalization condition. For a given value of  $d$ , magnitude squared of the wave function is simply

$$\psi^*\psi = A^2e^{-\frac{x^2}{d^2}},$$

a Gaussian distribution centered at 0 with standard deviation  $d$ . This means that a particle with this wavefunction has a maximum probability of being found at the origin, and diminishing but non-vanishing probabilities of being found at points farther from the origin.

## 4 Operators

Since our wavefunctions are given as functions of position, the Born rule immediately gives information about the position of a particle from its wavefunction. However, if the wavefunction is to fully describe a particle, it must also contain information such as the momentum. We already determined in our “derivation” of the Schrödinger equation that, for certain  $\psi$ ,

$$p\psi = -i\hbar\nabla\psi;$$

we use this to define the momentum operator

$$\hat{p} = -i\hbar\nabla.$$

The hat indicates that  $\hat{p}$  is an operator which, for eigenvectors  $\psi_p$ , has the property that  $\hat{p}\psi_p$  is proportional to  $p\psi_p$ , where  $p$  is the real value of the momentum. Another example of an operator is the Hamiltonian

$$\hat{H} = \frac{\hbar^2\nabla^2}{2m} - V(\mathbf{r}).$$

The time-independent Schrödinger equation simply states that the eigenvalues of this operator are the physical energy values for the system.

We can use operators to extract more information about the system from the wavefunction. For example, we can determine the expected value of the momentum for the Gaussian wavepacket. The expected value of an operator  $O$  is given by

$$\langle O \rangle = \int \psi^* O \psi d\tau.$$

Therefore, the average value of the momentum for the wavepacket is

$$\langle \hat{p} \rangle = \int_{-\infty}^{\infty} \left( Ae^{-\frac{x^2}{2d^2}} \right) \left( -i\hbar A \frac{x}{d^2} e^{-\frac{x^2}{2d^2}} \right) dx = -i\hbar \frac{A^2}{d^2} \int_{-\infty}^{\infty} x e^{-\frac{x^2}{d^2}} dx = 0.$$

We know the integral vanishes because the integrand is odd. As a more interesting example, we may consider the expected value of the momentum squared. The operator we need to use is simply

$$\hat{p}^2 = -\hbar^2 \frac{\partial^2}{\partial x^2}.$$

We can determine that

$$\hat{p}^2\psi(x) = -A\hbar^2 \left( \frac{x^2 - d^2}{d^4} \right) e^{-\frac{x^2}{2d^2}}$$

so that the expected value is

$$\langle \hat{p}^2 \rangle = -\frac{A^2 \hbar^2}{d^4} \int_{-\infty}^{\infty} (x^2 - d^2) e^{-\frac{x^2}{d^2}} dx$$

Upon evaluating the integral, we have

$$\langle \hat{p}^2 \rangle = \frac{\hbar^2 \sqrt{\pi}}{2} \frac{A^2}{d}$$

To give meaning to this result, we need to determine the relationship between  $A$  and  $d$ . The normalization condition tells us that

$$A^2 \int_{-\infty}^{\infty} e^{-\frac{x^2}{d^2}} dx = 1.$$

The integral is  $d\sqrt{\pi}$ , so we have

$$A^2 = \frac{1}{d\sqrt{\pi}}.$$

Substituting into the previous result, we have

$$\langle \hat{p}^2 \rangle = \frac{\hbar^2}{2d^2}.$$

This is a manifestation of a quantum effect known as *confinement energy*. When  $d$ , the scale of the space in which the particle is confined, becomes very small, the expected value of  $p^2$  (and therefore the energy) becomes very large.

Operators in quantum mechanics have a special property: they are all Hermitian. Hermitian operators are easier to define in Heisenberg's formulation of quantum mechanics than in Schrödinger's; in the Schrödinger formulation, an operator  $H$  is Hermitian if

$$\int \psi_1^* H \psi_2 d\tau = \int (H \psi_1)^* \psi_2 d\tau$$

for any  $\psi_1$  and  $\psi_2$ . Hermitian operators have all real eigenvalues and orthogonal eigenvectors. The fact that they have real eigenvalues is important because it means that they can correspond to physical values; we will employ the orthogonality of the eigenvectors in later lectures.

## 5 Problems

1. Determine  $\langle \hat{x}^2 \rangle - \langle \hat{x} \rangle^2$  and  $\langle \hat{p}^2 \rangle - \langle \hat{p} \rangle^2$  for the Gaussian wavepacket. These quantities are  $\Delta x^2$  and  $\Delta p^2$ , respectively. Can this product ever be zero?
2. Even if the wavefunction is normalized at a given time, we have not yet assured that it will be normalized throughout time; i.e., we have not proved the conservation of probability. Define  $\rho = \psi^* \psi$  as the probability density; show that if

$$\nabla \cdot \mathbf{j} + \frac{d\rho}{dt} = 0,$$

then the probability current  $\mathbf{j}$  is

$$\mathbf{j} = \frac{\hbar}{2mi} [\psi^* (\nabla \psi) + \psi (\nabla \psi^*)]$$

3. Solve the Schrödinger equation for a “particle in a box”; that is, a particle confined by a potential which is 0 for  $|x| < a$  and infinity elsewhere.