

SCHRÖDINGER EQUATION

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The Schrödinger equation is the heart of non-relativistic quantum mechanics, in that virtually all the physics is derived from its solutions in various systems. The origin of the equation is difficult to pin down, as every book on introductory quantum mechanics has its own way of introducing it. At one extreme is Griffiths's book, in which he simply states the equation on page 1 and says nothing more about where it came from. At the other extreme, Volume 3 of Feynman's lectures doesn't introduce the equation until about two-thirds of the way through the book. Somewhere in the middle are the volumes by Landau & Lifshitz and Shankar, where a mathematical introduction to operators precedes the Schrödinger equation itself.

In fact, there is no way to derive, at least in a strict mathematical sense, the Schrödinger equation. It is based mostly on physical intuition and some truly remarkable insights (or, as some might less charitably say, guesses) made by pioneers such as Planck, Einstein, de Broglie, Heisenberg and, of course, Schrödinger himself.

The story of the genesis of the equation is told most memorably for me in the now-classic 1958 textbook by French physicist Albert Messiah. I'll sketch his discussion here, although the reader is referred to the original (still listed on Amazon as a Dover publication from 2014) for a more complete coverage.

The idea for quantum mechanics can be traced back to early ideas about electrons in atoms. If we consider the hydrogen atom as the simplest example, an electron was envisaged to be orbiting the central proton much as a planet orbits the Sun. There are several objections to this model, but perhaps the most serious is that, as is known from Maxwell's equations of electromagnetism, an accelerating charge radiates energy in the form of electromagnetic waves. An electron is, of course, charged, and if it moves in a circular orbit around the proton, it is accelerating (due to centripetal acceleration). Thus, the electron should lose energy due to radiation, which would cause its orbit to decay and thus it would spiral in to collide with the proton, meaning that hydrogen (and by extension, all atoms) would be unstable.

Another objection is that it is in practice impossible to measure the location of an electron without disturbing it. To measure the position of an

electron in an atom, we would need a measuring probe (usually, a photon) that is at least as small as the atom we are probing. Without going into specifics (it's an interesting calculation if you want to try it yourself), if we use a photon with a wavelength on the order of the size of a hydrogen atom, its energy is great enough to ionize the atom, so we would then have no idea where the electron is. If we try to use a photon of lower energy, this in turn means that its wavelength is longer, so the precision with which a measurement is made falls to the extent that we again have very limited knowledge of the location of the electron.

It was recognized that there is little point in constructing a physical theory based on measurements that are impossible, even in principle, to make.

In 1905, one of Einstein's 'annus mirabilis' papers proposed that light consisted of quanta (now known as photons). Together with Planck, he proposed that the energy E of a photon is related to its frequency ν by the equation

$$E = h\nu \quad (1)$$

where h is Planck's constant. The momentum p was proposed to be related to the wavelength λ by

$$p = \frac{h}{\lambda} \quad (2)$$

These relations are more commonly given as

$$\begin{aligned} E &= \hbar\omega \\ p &= \hbar k \end{aligned} \quad (3)$$

where

$$\hbar \equiv \frac{h}{2\pi} \quad (4)$$

$$\omega = 2\pi\nu \quad (5)$$

$$k = \frac{2\pi}{\lambda} \quad (6)$$

ω is the angular frequency (in radians per second) and k is the *wave number*.

At the time, these relations were assumed to apply only to electromagnetic radiation. De Broglie changed this in his Ph.D. thesis by proposing that *all* particles can also be viewed as waves, and that the same equations related the frequency, wavelength, energy and momentum of the particle. In particular, the electron can be viewed as a wave as well as a particle.

The next step involved writing down the expression for a wave travelling as a free particle. In general, we can write this in one dimension as a wave amplitude $\psi(x, t)$

$$\psi(x, t) = e^{i(kx - \omega t)} \quad (7)$$

We can see that this represents a wave with a phase velocity given by a location where the exponent is a constant (say, 0):

$$kx - \omega t = 0 \quad (8)$$

The velocity is then

$$\frac{dx}{dt} = \frac{\omega}{k} \quad (9)$$

In practice, a particle is actually composed of a superposition of a number of waves of varying wavelength, forming a *wave packet*, and the velocity of the particle is the *group velocity* of the wave packet rather than the phase velocity of a single wave, but for our purposes, we'll leave that complication for later.

Using 3, we can write

$$\psi(x, t) = e^{i(px - Et)/\hbar} \quad (10)$$

For a non-relativistic free particle of mass m , we have

$$E = \frac{p^2}{2m} \quad (11)$$

Now we want an equation whose solution is 10, but we also want it to satisfy certain conditions.

First, we postulate that, if we know $\psi(x, t)$ at some time t , then we should be able to predict its behaviour at all future times. This means that if the desired equation is a differential equation, the time derivative must be a first derivative, since the solution of a first order differential equation requires only the specification of a single initial (or boundary) condition. For comparison, Newton's equation of motion $F = ma = m \frac{d^2x}{dt^2}$ is a *second-order* equation, and its solution requires an initial condition for both the position x and the velocity $\frac{dx}{dt}$.

Another postulate is that the equation should be linear, so that if we have two independent solutions of the same equation, any linear combination (such as a sum) of the solutions is also a solution. Derivatives are linear operators, so the equation may contain various derivatives. However, an operator S that returns the square of a function is *not* linear, since, for example

$$S(f + g) = (f + g)^2 \neq f^2 + g^2 = Sf + Sg \quad (12)$$

Let's get back to 10 and try applying various derivatives to it. For the first-order time derivative we have

$$\frac{\partial \psi}{\partial t} = -\frac{i}{\hbar} E e^{i(px-Et)/\hbar} \quad (13)$$

which we can rewrite as

$$i\hbar \frac{\partial \psi}{\partial t} = E e^{i(px-Et)/\hbar} = E\psi \quad (14)$$

The other independent variable which can be used to write derivatives is x , so we try the first-order derivative with respect to x :

$$\frac{\partial \psi}{\partial x} = \frac{ip}{\hbar} e^{i(px-Et)/\hbar} \quad (15)$$

or

$$\frac{\hbar}{i} \frac{\partial \psi}{\partial x} = p e^{i(px-Et)/\hbar} = p\psi \quad (16)$$

Finally, we can take the second derivative with respect to x by applying the operator $\frac{\hbar}{i} \frac{\partial}{\partial x}$ to 16:

$$-\hbar^2 \frac{\partial^2 \psi}{\partial x^2} = p^2 e^{i(px-Et)/\hbar} \quad (17)$$

$$= 2mE e^{i(px-Et)/\hbar} = 2mE\psi \quad (18)$$

where we used 11 to get the last line.

Combining 14 and 18 we get

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}} \quad (19)$$

This is Schrödinger's equation for a free particle.

We haven't actually *derived* this equation, since it was based on several postulates and inspired guesses about the wave nature of particles.

Since free particles aren't particularly interesting in real life, we need to generalize 19 to the case where the particle is subject to a potential. Messiah presents a rather hand-waving argument in his §II.13 which you can look up if you like. The end result is that we assume that a scalar potential $V(x)$ can just be added into the operator on the RHS of 19, so we get the Schrödinger equation for a particle moving in a scalar potential:

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x) \psi} \quad (20)$$

The combined operator on the RHS is interpreted as kinetic + potential energy operating on ψ . Berman just asserts that this is the Schrödinger equation for a particle moving in a potential.

Finally, it's worth noting that this argument gives us a recipe for converting physical quantities into quantum mechanical operators. From 14 we have

$$E \rightarrow i\hbar \frac{\partial}{\partial t} \quad (21)$$

and from 16 we have

$$p \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x} \quad (22)$$

We can generalize the above arguments to three dimensions by replacing px by $\mathbf{p} \cdot \mathbf{r}$ where \mathbf{p} is the 3-dim momentum vector and \mathbf{r} is the 3-dim position vector. We then get $E = \mathbf{p}^2/2m$ and

$$\boxed{i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r}) \psi} \quad (23)$$

and, for the momentum operator

$$\mathbf{p} \rightarrow \frac{\hbar}{i} \nabla \quad (24)$$

REFERENCES AND FURTHER READING

- (1) Griffiths, David J. (2005), *Introduction to Quantum Mechanics*, 2nd Edition; Pearson Education, Chapter 1.
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- (4) Shankar, R. (1994), *Principles of Quantum Mechanics*, Plenum Press, Chapters 3 & 4.
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