

# Schrödinger equation

In physics, specifically quantum mechanics, the **Schrödinger equation**, formulated in 1926 by Austrian physicist Erwin Schrödinger, is an equation that describes how the quantum state of a physical system changes in time. It is as central to quantum mechanics as Newton's laws are to classical mechanics.

$E\Psi = \hat{H}\Psi$
$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$
Two forms of the Schrödinger equation

In the standard interpretation of quantum mechanics, the quantum state, also called a wavefunction or state vector, is the most complete description that can be given to a physical system. Solutions to Schrödinger's equation describe not only molecular, atomic and subatomic systems, but also macroscopic systems, possibly even the whole universe. [1]

The most general form is the time-dependent Schrödinger equation, which gives a description of a system evolving with time. For systems in a stationary state, (i.e. where the Hamiltonian is not explicitly dependent on time) the time-independent Schrödinger equation is sufficient. Approximate solutions to the time-independent Schrödinger equation are commonly used to calculate the energy levels and other properties of atoms and molecules.

Schrödinger's equation can be mathematically transformed into Werner Heisenberg's matrix mechanics, and into Richard Feynman's path integral formulation. The Schrödinger equation describes time in a way that is inconvenient for relativistic theories, a problem which is not as severe in matrix mechanics and completely absent in the path integral formulation.

## The Schrödinger equation

The Schrödinger equation takes several different forms, depending on the physical situation. This section presents the equation for the general case and for the simple case encountered in many textbooks.

### General quantum system

For a general quantum system: [2]

$$i\hbar\frac{\partial}{\partial t}\Psi = \hat{H}\Psi$$

where

- $\Psi$  is the wave function; the probability amplitude for different configurations of the system at different times,
- $i\hbar\frac{\partial}{\partial t}$  is the energy operator (  $i$  is the imaginary unit and  $\hbar$  is the reduced Planck constant),
- $\hat{H}$  is the Hamiltonian operator.

## Single particle in a potential

For a single particle with potential energy  $V$  in position space, the Schrödinger equation takes the form:<sup>[3]</sup>

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

where

- $-\frac{\hbar^2}{2m} \nabla^2$  is the kinetic energy operator, where  $m$  is the mass of the particle.
- $\nabla^2$  is the Laplace operator. In three dimensions, the Laplace operator is  $\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$ , where  $x$ ,  $y$ , and  $z$  are the Cartesian coordinates of space.
- $V(\mathbf{r})$  is the time-independent potential energy at the position  $\mathbf{r}$ .
- $\Psi(\mathbf{r}, t)$  is the probability amplitude for the particle to be found at position  $\mathbf{r}$  at time  $t$ .
- $\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r})$  is the Hamiltonian operator for a single particle in a potential.

## Time independent or stationary equation

The time independent equation, again for a single particle with potential energy  $V$ , takes the form:<sup>[4]</sup>

$$E\psi(r) = -\frac{\hbar^2}{2m} \nabla^2 \psi(r) + V(r)\psi(r)$$

This equation describes the standing wave solutions of the time-dependent equation, which are the states with definite energy.

## Historical background and development

Following Max Planck's quantization of light (see black body radiation), Albert Einstein interpreted Planck's quantum to be photons, particles of light, and proposed that the energy of a photon is proportional to its frequency, one of the first signs of wave–particle duality. Since energy and momentum are related in the same way as frequency and wavenumber in special relativity, it followed that the momentum  $p$  of a photon is proportional to its wavenumber  $k$ .

$$p = \frac{h}{\lambda} = \hbar k$$

Louis de Broglie hypothesized that this is true for all particles, even particles such as electrons. Assuming that the waves travel roughly along classical paths, he showed that they form standing waves for certain discrete frequencies. These correspond to discrete energy levels, which reproduced the old quantum condition.<sup>[5]</sup>

Following up on these ideas, Schrödinger decided to find a proper wave equation for the electron. He was guided by William R. Hamilton's analogy between mechanics and optics, encoded in the observation that the zero-wavelength limit of optics resembles a mechanical system—the trajectories of light rays become sharp tracks which obey Fermat's principle, an analog of the principle of least action.<sup>[6]</sup> A modern version of his reasoning is reproduced in the next section. The equation he found is:

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

Using this equation, Schrödinger computed the hydrogen spectral series by treating a hydrogen atom's electron as a wave  $\Psi(x, t)$ , moving in a potential well  $V$ , created by the proton. This computation accurately reproduced the energy levels of the Bohr model.

However, by that time, Arnold Sommerfeld had refined the Bohr model with relativistic corrections.<sup>[7]</sup> <sup>[8]</sup> Schrödinger used the relativistic energy momentum relation to find what is now known as the Klein–Gordon

equation in a Coulomb potential (in natural units):

$$\left(E + \frac{e^2}{r}\right)^2 \psi(x) = -\nabla^2 \psi(x) + m^2 \psi(x).$$

He found the standing waves of this relativistic equation, but the relativistic corrections disagreed with Sommerfeld's formula. Discouraged, he put away his calculations and secluded himself in an isolated mountain cabin with a lover.<sup>[9]</sup>

While at the cabin, Schrödinger decided that his earlier non-relativistic calculations were novel enough to publish, and decided to leave off the problem of relativistic corrections for the future. He put together his wave equation and the spectral analysis of hydrogen in a paper in 1926.<sup>[10]</sup> The paper was enthusiastically endorsed by Einstein, who saw the matter-waves as an intuitive depiction of nature, as opposed to Heisenberg's matrix mechanics, which he considered overly formal.<sup>[11]</sup>

The Schrödinger equation details the behaviour of  $\psi$  but says nothing of its *nature*. Schrödinger tried to interpret it as a charge density in his fourth paper, but he was unsuccessful.<sup>[12]</sup> In 1926, just a few days after Schrödinger's fourth and final paper was published, Max Born successfully interpreted  $\psi$  as a probability amplitude.<sup>[13]</sup> Schrödinger, though, always opposed a statistical or probabilistic approach, with its associated discontinuities—much like Einstein, who believed that quantum mechanics was a statistical approximation to an underlying deterministic theory—and never reconciled with the Copenhagen interpretation.<sup>[14]</sup>

## Derivation

### Short heuristic derivation

Schrödinger's equation can be derived in the following short heuristic way. It should be noted that Schrödinger's wave equation was a result of the ingenious mathematical intuition of Erwin Schrödinger, and cannot be derived independently.

#### Assumptions

1. The total energy  $E$  of a particle is

$$E = T + V = \frac{p^2}{2m} + V.$$

This is the classical expression for a particle with mass  $m$  where the total energy  $E$  is the sum of the kinetic energy  $T$ , and the potential energy  $V$  (which can vary with position, and time).  $p$  and  $m$  are respectively the momentum and the mass of the particle.

2. Einstein's light quanta hypothesis of 1905, which asserts that the energy  $E$  of a photon is proportional to the frequency  $\nu$  (or angular frequency,  $\omega = 2\pi\nu$ ) of the corresponding electromagnetic wave:

$$E = h\nu = \hbar\omega,$$

3. The de Broglie hypothesis of 1924, which states that any particle can be associated with a wave, and that the momentum  $p$  of the particle is related to the wavelength  $\lambda$  (or wavenumber  $k$ ) of such a wave by:

$$p = \frac{h}{\lambda} = \hbar k,$$

Expressing  $\mathbf{p}$  and  $\mathbf{k}$  as vectors, we have

$$\mathbf{p} = \hbar\mathbf{k}.$$

4. The three assumptions above allow one to derive the equation for plane waves only. To conclude that it is true in general requires the superposition principle, and thus, one must separately postulate that the Schrödinger equation is linear.

### Expressing the wave function as a complex plane wave

Schrödinger's idea was to express the phase of a plane wave as a complex phase factor:

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

and to realize that since

$$\frac{\partial}{\partial t}\Psi = -i\omega\Psi$$

then

$$E\Psi = \hbar\omega\Psi = i\hbar\frac{\partial}{\partial t}\Psi$$

and similarly since

$$\frac{\partial}{\partial x}\Psi = ik_x\Psi$$

and

$$\frac{\partial^2}{\partial x^2}\Psi = -k_x^2\Psi$$

we find:

$$p_x^2\Psi = (\hbar k_x)^2\Psi = -\hbar^2\frac{\partial^2}{\partial x^2}\Psi$$

so that, again for a plane wave, he obtained:

$$p^2\Psi = (p_x^2 + p_y^2 + p_z^2)\Psi = -\hbar^2\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)\Psi = -\hbar^2\nabla^2\Psi$$

And, by inserting these expressions for the energy and momentum into the classical formula we started with, we get Schrödinger's famed equation, for a single particle in the 3-dimensional case in the presence of a potential  $V$ :

$$i\hbar\frac{\partial}{\partial t}\Psi = -\frac{\hbar^2}{2m}\nabla^2\Psi + V\Psi$$

## Versions

There are several equations that go by Schrödinger's name:

### Time dependent equation

This is the equation of motion for the quantum state. In the most general form, it is written:<sup>[15]</sup>

$$i\hbar\frac{\partial}{\partial t}\Psi(x, t) = \hat{H}\Psi(x, t)$$

where  $\hat{H}$  is a linear operator acting on the wavefunction  $\Psi$ . For the specific case of a single particle in one dimension moving under the influence of a potential  $V$ .<sup>[15]</sup>

$$i\hbar\frac{\partial}{\partial t}\Psi(x, t) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\Psi(x, t) + V(x)\Psi(x, t)$$

and the operator  $\hat{H}$  can be read off:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x).$$

For a particle in three dimensions, the only difference is more derivatives:

$$i\hbar\frac{\partial}{\partial t}\Psi(x, y, z, t) = -\frac{\hbar^2}{2m}\nabla^2\Psi(x, y, z, t) + V(x, y, z)\Psi(x, y, z, t)$$

and for  $N$  particles, the difference is that the wavefunction is in  $3N$ -dimensional configuration space, the space of all possible particle positions.<sup>[16]</sup>

$$i\hbar \frac{\partial}{\partial t} \Psi(x_1, \dots, x_n, t) = \hbar^2 \left( -\frac{\nabla_1^2}{2m_1} - \frac{\nabla_2^2}{2m_2} \dots - \frac{\nabla_N^2}{2m_N} \right) \Psi(x_1, \dots, x_n, t) + V(x_1, \dots, x_n, t) \Psi(x_1, \dots, x_n, t).$$

This last equation is in a very high dimension, so that the solutions are not easy to visualize.

### Time independent equation

This is the equation for the standing waves, the eigenvalue equation for  $\hat{H}$ . The time independent Schrödinger equation can be obtained from the time dependent version by assuming a trivial time dependence of the wavefunction of the form  $\Psi(x, t) = \psi(x)e^{-iEt/\hbar}$ .<sup>[17]</sup> This is possible only if the Hamiltonian is not an explicit function of time, as otherwise the equation is not separable into its spatial and temporal parts. The operator  $i\hbar \frac{\partial}{\partial t}$  can then be replaced by  $E$ . In abstract form, for a general quantum system, it is written:<sup>[15]</sup>

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

For a particle in one dimension,

$$E\psi = -\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2} + V(x)\psi.$$

But there is a further restriction—the solution must not grow at infinity, so that it has either a finite  $L^2$ -norm (if it is a bound state) or a slowly diverging norm (if it is part of a continuum):<sup>[18]</sup>

$$\|\psi\|^2 = \int |\psi(x)|^2 dx.$$

For example, when there is no potential, the equation reads:<sup>[19]</sup>

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

which has oscillatory solutions for  $E > 0$  (the  $C_n$  are arbitrary constants):

$$\psi_E(x) = C_1 e^{i\sqrt{2mE/\hbar^2} x} + C_2 e^{-i\sqrt{2mE/\hbar^2} x}$$

and exponential solutions for  $E < 0$

$$\psi_{-|E|}(x) = C_1 e^{\sqrt{2m|E|/\hbar^2} x} + C_2 e^{-\sqrt{2m|E|/\hbar^2} x}.$$

The exponentially growing solutions have an infinite norm, and are not physical. They are not allowed in a finite volume with periodic or fixed boundary conditions.

For a constant potential  $V$  the solution is oscillatory for  $E > V$  and exponential for  $E < V$ , corresponding to energies which are allowed or disallowed in classical mechanics. Oscillatory solutions have a classically allowed energy and correspond to actual classical motions, while the exponential solutions have a disallowed energy and describe a small amount of quantum bleeding into the classically disallowed region, to quantum tunneling. If the potential  $V$  grows at infinity, the motion is classically confined to a finite region, which means that in quantum mechanics every solution becomes an exponential far enough away. The condition that the exponential is decreasing restricts the energy levels to a discrete set, called the allowed energies.

## Nonlinear equation

The nonlinear Schrödinger equation is the partial differential equation (in dimensionless form)<sup>[20]</sup>

$$i\partial_t\psi = -\frac{1}{2}\partial_x^2\psi + \kappa|\psi|^2\psi$$

for the complex field  $\psi(x,t)$ .

This equation arises from the Hamiltonian<sup>[20]</sup>

$$H = \int dx \left[ \frac{1}{2}|\partial_x\psi|^2 + \frac{\kappa}{2}|\psi|^4 \right]$$

with the Poisson brackets

$$\begin{aligned} \{\psi(x), \psi(y)\} &= \{\psi^*(x), \psi^*(y)\} = 0 \\ \{\psi^*(x), \psi(y)\} &= i\delta(x-y). \end{aligned}$$

It must be noted that this is a classical field equation. Unlike its linear counterpart, it never describes the time evolution of a quantum state.

## Properties

The Schrödinger equation has certain properties.

### Local conservation of probability

The probability density of a particle is  $\Psi^*(x, t)\Psi(x, t)$ . The probability flux is defined as [in units of (probability)/(area  $\times$  time)]:

$$\mathbf{j} = -\frac{i\hbar}{2m} (\Psi^*\nabla\Psi - \Psi\nabla\Psi^*) = \frac{\hbar}{m} \text{Im}(\Psi^*\nabla\Psi).$$

The probability flux satisfies the continuity equation:

$$\frac{\partial}{\partial t}P(x, t) + \nabla \cdot \mathbf{j} = 0$$

where  $P(x, t)$  is the probability density [measured in units of (probability)/(volume)]. This equation is the mathematical equivalent of the probability conservation law.

For a plane wave:

$$\begin{aligned} \Psi(x, t) &= Ae^{i(kx - \omega t)} \\ j(x, t) &= |A|^2 \frac{\hbar k}{m}. \end{aligned}$$

So that not only is the probability of finding the particle the same everywhere, but the probability flux is as expected from an object moving at the classical velocity  $p/m$ . The reason that the Schrödinger equation admits a probability flux is because all the hopping is local and forward in time.

## Relativity

The Schrödinger equation does not take into account relativistic effects; as a wave equation, it is invariant under a Galilean transformation, but not under a Lorentz transformation. But in order to include relativity, the physical picture must be altered.

The Klein–Gordon equation uses the relativistic mass-energy relation:

$$E^2 = p^2 c^2 + m^2 c^4$$

to produce the differential equation:

$$-\frac{1}{c^2} \frac{\partial^2}{\partial t^2} \psi = -\nabla^2 \psi + \frac{m^2 c^2}{\hbar^2} \psi$$

which is relativistically invariant.

## Solutions

Some general techniques are:

- Perturbation theory
- The variational method
- Quantum Monte Carlo methods
- Density functional theory
- The WKB approximation and semi-classical expansion

In some special cases, special methods can be used:

- List of quantum-mechanical systems with analytical solutions
- Hartree-Fock method and post Hartree-Fock methods
- Discrete delta-potential method

## Notes

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- [13] Moore, W.J. (1992). *Schrödinger: Life and Thought*. Cambridge University Press. p. 220. ISBN 0-521-43767-9.
- [14] It is clear that even in his last year of life, as shown in a letter to Max Born, that Schrödinger never accepted the Copenhagen interpretation. cf p. 220 Moore, W.J. (1992). *Schrödinger: Life and Thought*. Cambridge University Press. p. 479. ISBN 0-521-43767-9.
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## External links

- Quantum Physics ([http://www.lightandmatter.com/html\\_books/0sn/ch13/ch13.html](http://www.lightandmatter.com/html_books/0sn/ch13/ch13.html)) - a textbook with a treatment of the time-independent Schrödinger equation
- Linear Schrödinger Equation (<http://eqworld.ipmnet.ru/en/solutions/lpde/lpde108.pdf>) at EqWorld: The World of Mathematical Equations.
- Nonlinear Schrödinger Equation (<http://eqworld.ipmnet.ru/en/solutions/npde/npde1403.pdf>) at EqWorld: The World of Mathematical Equations.
- The Schrödinger Equation in One Dimension (<http://www.colorado.edu/UCB/AcademicAffairs/ArtsSciences/physics/TZD/PageProofs1/TAYL07-203-247.I.pdf>) as well as the directory of the book (<http://www.colorado.edu/UCB/AcademicAffairs/ArtsSciences/physics/TZD/PageProofs1/>).
- All about 3D Schrödinger Equation (<http://hyperphysics.phy-astr.gsu.edu/hbase/hframe.html>)
- Mathematical aspects of Schrödinger equations are discussed on the Dispersive PDE Wiki ([http://tosio.math.toronto.edu/wiki/index.php/Main\\_Page](http://tosio.math.toronto.edu/wiki/index.php/Main_Page)).
- Web-Schrödinger: Interactive solution of the 2D time dependent Schrödinger equation (<http://www.nanotechnology.hu/online/web-schroedinger/index.html>)
- An alternate derivation of the Schrödinger Equation (<http://behindtheguesses.blogspot.com/2009/06/schrodinger-equation-corrections.html>)
- Online software- Periodic Potential Lab (<http://nanohub.org/resources/3847>) Solves the time independent Schrödinger equation for arbitrary periodic potentials.

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