Schrödinger equation

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In physics, the **Schrödinger equation**, proposed by the Austrian physicist Erwin Schrödinger in 1926, describes the space- and time-dependence of quantum mechanical systems. It is of central importance in non-relativistic quantum mechanics, playing a role for microscopic particles analogous to Newton's second law in classical mechanics for macroscopic particles. Microscopic particles include elementary particles, such as electrons, as well as systems of particles, such as atomic nuclei. Macroscopic particles vary in mass from cells to the galactic superclusters.

Quantum physics

$$\Delta x\, \Delta p \ge \frac{\hbar}{2}$$

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Historical background and development

Schrödinger's equation follows very naturally from earlier developments:

In 1905, by considering the photoelectric effect, Albert Einstein had published his

$$E = hf$$

formula for the relation between the energy **E** and frequency **f** of the quanta of radiation (photons), where **h** is Planck's constant.

In 1924 Louis de Broglie presented his de Broglie hypothesis which states that *all* particles (not just photons) have an associated wavefunction ψ with properties:

> $p = h/\lambda$, where λ is the wavelength of the wave and **p** the momentum of the particle.

De Broglie showed that this was consistent with Einstein's formula and special relativity so that

$$E = hf$$

still holds, but now this is hypothesized to hold for *all* particles, not just photons anymore.

Expressed in terms of angular frequency $\omega = 2\pi f$ and wavenumber $k = 2\pi/\lambda$, with $\hbar = h/2\pi$ we get:

$$E = \hbar\omega$$

and

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

where we have expressed p and k as vectors.

Schrödinger's great insight, late in 1925, was to express the phase of a plane wave as a complex phase factor:

$$\psi \approx \exp(i(\mathbf{k}\cdot\mathbf{x} - \omega t))$$

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:

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

then

$$p_x\psi = \hbar k_x\psi = -i\hbar\frac{\partial}{\partial x}\psi$$

and hence:

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

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

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

And by inserting these expressions into the Newtonian formula for a particle with total energy **E**, mass **m**, moving in a potential **V**:

$E = \frac{p^2}{2m} + V$ (simply the sum of the kinetic energy and potential energy; the plane wave model assumed **V** = 0)

he got his famed equation for a single particle in the 3-dimensional case in the presence of a potential:

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

Using this equation, Schrödinger computed the spectral lines for hydrogen by treating a hydrogen atom's single negatively charged electron as a wave, ψ, moving in a potential well, **V**, created by the positively charged proton. This computation tallied with experiment, the Bohr model and also the results of Werner Heisenberg's matrix mechanics - but without having to introduce Heisenberg's concept of non-commuting observables. Schrödinger published his wave equation and the spectral analysis of hydrogen in a series of four papers in 1926.

The Schrödinger equation defines the behaviour of ψ, but does not interpret what ψ *is*. Schrödinger tried unsuccessfully to interpret it as a charge density. In 1926 Max Born, just a few days after Schrödinger fourth and final paper was published, successfully interpreted ψ as a probability amplitude, although Schrödinger was never reconciled to this statistical or probabilistic approach.

Mathematical formulation

$$H(t)\,|\,\psi(t)\rangle = i\hbar\frac{d}{dt}\,|\,\psi(t)\rangle$$

In the mathematical formulation of quantum mechanics, a physical system is associated with a complex Hilbert space such that each instantaneous state of the system is described by a ray (a one-dimensional subspace) in that space. The nonzero elements of a Hilbert space are by definition normalizable and it is convenient, although not necessary, to represent a state by an element of the ray which is normalized to unity. This vector is often somewhat loosely referred to as wave function, although in a more rigorous formulation of quantum mechanics a wave function is a special case of a state vector. (In fact, a wave function is a state in the position representation, see below). A state vector encodes the probabilities for the outcomes of all possible measurements applied to the system. It contains all information of the system that is knowable in a quantum mechanical sense. As the state of a system generally changes over time, the state vector is a function of time. The Schrödinger equation provides a quantitative description of the rate of change of the state vector.

In Dirac's bra-ket notation at time *t* the state is given by the *ket* $|\psi(t)\rangle$. The time-dependent Schrödinger equation, giving the time evolution of the ket, is:

$$H(t)\left|\psi\left(t\right)\right\rangle = \mathrm{i}\hbar\frac{d}{dt}\left|\psi\left(t\right)\right\rangle$$

where i is the imaginary unit, *t* is time, *d* / *dt* is the derivative with respect to *t*, $\hbar$ is the reduced Planck's constant (Planck's constant divided by 2π), $\psi(t)$ is the time dependent state vector, and *H*(*t*) is the Hamiltonian (a self-adjoint operator acting on the state space). If one assumes a certain representation for ψ, for instance position or momentum representation, the state vector is assumed to depend on more variables than time alone, and the time derivative must be replaced by the partial derivative $\partial/\partial t$.

The Hamiltonian describes the total energy of the system. As with the force occurring in Newton's second law, its form is not provided by the Schrödinger equation, but must be independently determined from the physical properties of the system.

Time-independent Schrödinger equation

For many real-world problems the energy operator (*H*), does not depend on time. Then it can be shown that the *time-dependent* Schrödinger equation simplifies [1] to the *time-independent* Schrödinger equation, which has the well-known appearance $H\Psi = E\Psi$.

An example of a simple one-dimensional time-independent Schrödinger equation for a particle of mass *m*, moving in a potential *U(x)* is: [1]

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + U(x)\psi(x) = E\psi(x).$$

The analogous 3-dimensional time-independent equation is, [2]:

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r})\right]\psi(\mathbf{r}) = E\psi(\mathbf{r}),$$

or

$$-\frac{\hbar^2}{2m}\nabla^2\psi + (U-E)\psi = 0,$$

where ∇ is the del operator.

For every time-independent Hamiltonian, H, there exists a set of quantum states, $|\psi_n\rangle$, known as **energy eigenstates**, and corresponding real numbers E_n satisfying the eigenvalue equation,

$$H\left|\psi_n\right\rangle = E_n\left|\psi_n\right\rangle.$$

Such a state possesses a definite total energy, whose value E_n is the eigenvalue of the Hamiltonian. The corresponding eigenvector ψ_n is normalizable to unity. This eigenvalue equation is referred to as the **time-independent Schrödinger equation**. We purposely left out the variable(s) on which the *wavefunction* ψ_n depends. In the first example above it depends on the single variable x and in the second on x, y, and z—the components of the vector **r**. In both cases the Schrödinger equation has the same appearance, but its Hamilton operator is defined on different function (state, Hilbert) spaces. In the first example the function space consists of functions of one variable and in the second example the function space consists of functions of three variables.

Self-adjoint operators, such as the Hamiltonian, have the property that their eigenvalues are always real numbers, as we would expect, since the energy is a physically observable quantity. Sometimes *more than one* linearly independent state vector corresponds to the same energy E_n. If the maximum number of linearly independent eigenvectors corresponding to E_n equals k, we say that the energy level E_n is **k-fold degenerate.** When k=1 the energy level is called *non-degenerate*.

On inserting a solution of the time-independent Schrödinger equation into the full Schrödinger equation, we get

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\left|\psi_n\left(t\right)\right\rangle = E_n\left|\psi_n\left(t\right)\right\rangle.$$

It is relatively easy to solve this equation. One finds that the energy eigenstates (i.e., solutions of the time-independent Schrödinger equation) change as a function of time only trivially, namely, only by a complex phase:

$$\left|\psi\left(t\right)\right\rangle = \mathrm{e}^{-\mathrm{i}Et/\hbar}\left|\psi\left(0\right)\right\rangle.$$

It immediately follows that the *probability amplitude*,

$$\psi(t)^*\psi(t) = \mathrm{e}^{\mathrm{i}Et/\hbar}\mathrm{e}^{-\mathrm{i}Et/\hbar}\psi(0)^*\psi(0) = |\psi(0)|^2,$$

is time-independent. Because of a similar cancellation of phase factors in bra and ket, all average (expectation) values of time-independent observables (physical quantities) computed from $\psi(t)$ are time-independent.

Energy eigenstates are convenient to work with because they form a complete set of states. That is, the eigenvectors $\{|n\rangle\}$ form a basis for the state space. We introduced here the short-hand notation $|n\rangle = \psi_n$. Then any state vector that is a solution of the *time-dependent* Schrödinger equation (with a time-independent H) $\left|\psi\left(t\right)\right\rangle$ can be written as a linear superposition of energy eigenstates:

$$\left|\psi\left(t\right)\right\rangle = \sum_n c_n(t)\left|n\right\rangle \quad , \quad H\left|n\right\rangle = E_n\left|n\right\rangle \quad , \quad \sum_n \left|c_n\left(t\right)\right|^2 = 1.$$

(The last equation enforces the requirement that $\left|\psi\left(t\right)\right\rangle$, like all state vectors, may be normalized to a unit vector.) Applying the Hamiltonian operator to each side of the first equation, the time-dependent Schrödinger equation in the left-hand side and using the fact that the energy basis vectors are by definition linearly independent, we readily obtain

$$\mathrm{i}\hbar\frac{\partial c_n}{\partial t} = E_n c_n\left(t\right).$$

Therefore, if we know the decomposition of $\left|\psi\left(t\right)\right\rangle$ into the energy basis at time t = 0, its value at any subsequent time is given simply by

$$|\psi(t)\rangle = \sum_n \mathrm{e}^{-\mathrm{i}E_n t/\hbar} c_n(0)\,|n\rangle\,.$$

Note that when some values $c_n(0)$ are not equal to zero for differing energy values E_n, the left-hand side is *not* an eigenvector of the energy operator *H*. The left-hand *is* an eigenvector when the only $c_n(0)$-values not equal to zero belong the same energy, so that $\mathrm{e}^{-\mathrm{i}E_n t/\hbar}$ can be factored out. In many real-world application this is the case and the state vector $\psi(t)$ (containing time only in its phase factor) is then a solution of the time-independent Schrödinger equation.

Example

Let $|\,1\,\rangle$ and $|\,2\,\rangle$ be degenerate eigenstates of the time-*independent* Hamiltonian H:

$$H\,|\,1\,\rangle = E|\,1\,\rangle \quad \text{and} \quad H\,|\,2\,\rangle = E|\,2\,\rangle.$$

Suppose a solution $\psi(t)$ of the full (time-*dependent*) Schrödinger equation of H has the form at *t = 0*:

$$|\,\psi(0)\,\rangle = c_1|\,1\,\rangle + c_2|\,2\,\rangle.$$

Hence, because of the discussion above, at *t > 0* :

$$|\,\psi(t)\,\rangle = \mathrm{e}^{-\mathrm{i}Et/\hbar}c_1|\,1\,\rangle + \mathrm{e}^{-\mathrm{i}Et/\hbar}c_2|\,2\,\rangle = \mathrm{e}^{-\mathrm{i}Et/\hbar}\left(c_1|\,1\,\rangle + c_2|\,2\,\rangle\right) = \mathrm{e}^{-\mathrm{i}Et/\hbar}|\,\psi(0)\,\rangle,$$

which shows that $\psi(t)$ only depends on time in a trivial way (through its phase), also in the case of degeneracy.

Apply now H:

$$H\,|\,\psi(t)\,\rangle = \mathrm{e}^{-\mathrm{i}Et/\hbar}c_1E\,|\,1\,\rangle + \mathrm{e}^{-\mathrm{i}Et/\hbar}c_2E\,|\,2\,\rangle = E\mathrm{e}^{-\mathrm{i}Et/\hbar}\left(c_1|\,1\,\rangle + c_2|\,2\,\rangle\right)$$

$$= E\mathrm{e}^{-\mathrm{i}Et/\hbar}|\,\psi(0)\,\rangle = E\,|\,\psi(t)\,\rangle.$$

Conclusion: The wavefunction $\psi(t)$ with the given initial condition (its form at *t* = 0), remains a solution of the time-*independent* Schrödinger equation $H\psi(t) = E\psi(t)$ for all times *t > 0*.

Footnote

1. ^ In fact also an initial condition must be used here. At time zero the wavefunction must be an eigenstate of *H*.

Schrödinger wave equation

The state space of certain quantum systems can be spanned with a **position basis**. In this situation, the Schrödinger equation may be conveniently reformulated as a partial differential equation for a wavefunction, a complex scalar field that depends on position as well as time. This form of the Schrödinger equation is referred to as the **Schrödinger wave equation**.

Elements of the position basis are called position eigenstates. We will consider only a single-particle system, for which each position eigenstate may be denoted by $|\mathbf{r}\rangle$, where the label $\mathbf{r}$ is a real vector. This is to be interpreted as a state in which the particle is localized at position $\mathbf{r}$. In this case, the state space is the space of all square-integrable complex functions.

The wave function

We define the wave function as the *projection* of the state vector $|\psi(t)\rangle$ onto the position basis:

$$\psi(\mathbf{r}, t) \equiv \langle \mathbf{r}|\psi(t)\rangle\,.$$

Since the position eigenstates form a basis for the state space, the integral over all projection operators is the identity operator:

$$\int |\mathbf{r}\rangle \langle\mathbf{r}|\, \mathrm{d}^3\mathbf{r} = \mathbf{I}.$$

This statement is called the resolution of the identity. With this, and the fact that kets have unit norm, we can show that

$$\begin{aligned}\langle\psi(t)|\psi(t)\rangle &= \langle\psi(t)| \left(\int |\mathbf{r}\rangle \langle\mathbf{r}|\, \mathrm{d}^3\mathbf{r}\right) |\psi(t)\rangle \\ &= \int \langle\psi(t)|\mathbf{r}\rangle \langle\mathbf{r}|\psi(t)\rangle \ \mathrm{d}^3\mathbf{r} \\ &= \int \psi(\mathbf{r},t)^* \ \psi(\mathbf{r},t) \ \mathrm{d}^3\mathbf{r} \\ &= 1\end{aligned}$$

where $\psi(\mathbf{r},t)^*$ denotes the complex conjugate of $\psi(\mathbf{r},t)$. This important result tells us that the absolute square of the wave function, integrated over all space, must be equal to 1:

$$\int |\psi(\mathbf{r},t)|^2 \ \mathrm{d}^3\mathbf{r} = 1.$$

We can thus interpret the absolute square of the wave function as the *probability density* for the particle to be found at each point in space. In other words, $|\psi(\mathbf{r},t)|^2 \mathrm{d}^3\mathbf{r}$ is the probability, at time *t*, of finding the particle in the infinitesimal region of volume $\mathrm{d}^3\mathbf{r}$ surrounding the position $\mathbf{r}$.

We have previously shown that energy eigenstates vary only by a complex phase as time progresses. Therefore, the absolute square of their wave functions do not change with time. Energy eigenstates thus correspond to static probability distributions.

Operators in the position basis

Any operator *A* acting on the wave function is defined in the position basis by

$$A\psi(\mathbf{r},t) \equiv \langle\mathbf{r}|A|\psi(t)\rangle\,.$$

The operators *A* on the two sides of the equation are different things: the one on the right acts on kets, whereas the one on the left acts on scalar fields. It is common to use the same symbols to denote operators acting on kets and their projections onto a basis. Usually, the kind of operator to which one is referring is apparent from the context, but this is a possible source of confusion.

Using the position-basis notation, the Schrödinger equation can be written as

$$H\psi(\mathbf{r},t) = \mathrm{i}\hbar\frac{\partial}{\partial t}\psi(\mathbf{r},t)\,.$$

This form of the Schrödinger equation is the **Schrödinger wave equation**. It may appear that this is an ordinary differential equation, but in fact the Hamiltonian operator typically includes partial derivatives with respect to the position variable $\mathbf{r}$. This usually leaves us with a difficult linear partial differential equation to solve.

Non-relativistic Schrödinger wave equation

In non-relativistic quantum mechanics, the Hamiltonian of a particle can be expressed as the sum of two operators, one corresponding to kinetic energy and the other to potential energy. The Hamiltonian of a particle with no electric charge and no spin in this case is:

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

where

$T = \frac{p^2}{2m}$ is the **kinetic energy operator**,
m is the mass of the particle,
$\mathrm{p} = -\mathrm{i}\hbar\nabla$ is the **momentum operator**,
$V = V(\mathbf{r})$ is the **potential energy operator**,
V is a real scalar function of the position operator $\mathbf{r}$,
∇ is the gradient operator, and
∇^2 is the Laplace operator.

This is a commonly encountered form of the Schrödinger wave equation, though not the most general one. The corresponding time-independent equation is

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

The relativistic generalizations of this wave equation are the Dirac equation, Klein-Gordon equation, Proca equation, Maxwell equations etc, depending on spin and mass of the particle. See relativistic wave equations for details.

Probability currents

In order to describe how probability density changes with time, it is acceptable to define probability current or probability flux. The probability flux represents a flowing of probability across space.

For example, consider a Gaussian probability curve centered around x_0 with x_0 moving at speed v to the right. One may say that the probability is flowing toward right, i.e., there is a probability flux directed to the right.

The probability flux $\mathbf{j}$ is defined as:

$$\mathbf{j} = \frac{\hbar}{m} \cdot \frac{1}{2\mathrm{i}}\left(\psi^*\nabla\psi - \psi\nabla\psi^*\right) = \frac{\hbar}{m}\mathrm{Im}\left(\psi^*\nabla\psi\right)$$

and measured in units of (probability)/(area × time) = $r^{-2}t^{-1}$.

The probability flux satisfies a quantum continuity equation, i.e.:

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

where $P(x,t)$ is the probability density and measured in units of (probability)/(volume) = r^{-3}. This equation is the mathematical equivalent of probability conservation law.

It is easy to show that for a plane wave,

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

the probability flux is given by

$$j(x,t) = |A|^2\frac{k\hbar}{m}.$$

Solutions of the Schrödinger equation

Analytical solutions of the time-independent Schrödinger equation can be obtained for a variety of relatively simple conditions. These solutions provide insight into the nature of quantum phenomena and sometimes provide a reasonable approximation of the behavior of more complex systems (e.g., in statistical mechanics, molecular vibrations are often approximated as harmonic oscillators). Several of the more common analytical solutions can be found in the list of quantum mechanical systems with analytical solutions.

For many systems, however, there is no analytic solution to the Schrödinger equation. In these cases, one must resort to approximate solutions. Some of the common techniques are:

- Perturbation theory
- The variational principle underpins many approximate methods (like the popular Hartree-Fock method which is the basis of the post Hartree-Fock methods)
- Quantum Monte Carlo methods
- Density functional theory
- The WKB approximation
- discrete delta-potential method

See also

- Theoretical and experimental justification for the Schrödinger equation
- Schrödinger picture
- Basic quantum mechanics
- Quantum number
    - Principal quantum number
    - Angular momentum quantum number
    - Magnetic quantum number
    - Spin quantum number
- Dirac equation
- Schrödinger's cat
- Schrodinger field
- Klein-Gordon equation

References

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- E. Schrödinger, *Phys. Rev.* **28** (1926) p. 1049

Modern reviews

- David J. Griffiths (2004). *Introduction to Quantum Mechanics (2nd ed.)*. Prentice Hall. ISBN 013805326X.

External links

- Linear Schrödinger Equation at EqWorld: The World of Mathematical Equations.

- Nonlinear Schrödinger Equation at EqWorld: The World of Mathematical Equations.

- The Schrödinger Equation in One Dimension as well as the directory of the book.

- All about 3D Schrödinger Equation

- Mathematical aspects of Schrödinger equation's are discussed on the Dispersive PDE Wiki.

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