

# The Schroedinger equation

After Planck, Einstein, Bohr, de Broglie, and many others (but before Born), the time was ripe for a complete theory that could be applied to any problem involving nano-scale particles.

Apparently, it needed to produce wave solutions, so it needed to be a *wave equation*. The wave equation must produce wave solutions with  $E = h\nu$  and  $p = h/\lambda$ .

An example of wave equation comes from electromagnetics:

$$\frac{\partial^2 E_x}{\partial z^2} = \mu\epsilon \frac{\partial^2 E_x}{\partial t^2}$$

Wave equations were also familiar from the study of acoustics.

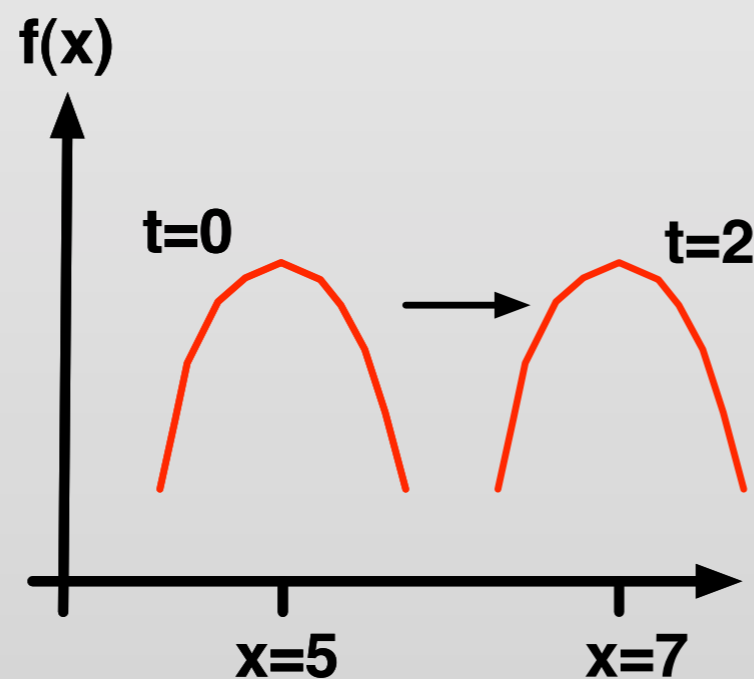
# A quick review of waves

A general form of a wave function can be written as

$$f(x - vt)$$

where  $x$  is position,  $t$  is time, and  $v$  is the wave velocity.  $f$  can be any function, in principle.

The motion of the function can be seen by keeping the argument of the function constant. Suppose the function had a peak where the argument is 5, i.e.  $f(5)$  is maximum point. The peak occurs wherever  $x - vt = 5$ . So as time progress (at  $t$  gets bigger), the point at which the peak occurs must move the right, in order to keep  $x - vt = 5$ .



Although, in principle, many different functions may be solutions to a wave equation, we often choose to work with harmonic functions, like sines and cosines. (We know from Fourier analysis that sines and cosines can be used to build up any other periodic function.)

$$\cos \left[ \frac{2\pi}{\lambda} (x - vt) \right]$$

This can be written in a form using wavelength and frequency

$$\cos \left( \frac{2\pi x}{\lambda} - 2\pi \nu t \right)$$

However, we will make frequent use of a form that includes a “wavenumber” and a radian frequency

$$\cos (kx - \omega t)$$

where  $k$  is the wavenumber  $= 2\pi/\lambda$  and  $\omega = 2\pi\nu$ . (Note the units.)

The function  $\cos(kx - \omega t)$  represents a wave traveling in the +x direction with velocity =  $\omega/k$ . This velocity is called the phase velocity, since it represents how fast a particular point of the wave is moving. Later, we'll encounter the "group velocity", which may be quite different from the phase velocity.

In 3-D space, the wave number turns into a wave-vector, denoting the direction of travel as well as the other info contained within the wave-number.

$$\vec{k} = k_x \vec{a}_x + k_y \vec{a}_y + k_z \vec{a}_z$$

The 3-D wave function would look like

$$f(\vec{r}, t) = \cos(\vec{k} \cdot \vec{r} - \omega t)$$

where the position vector is  $\vec{r} = x\vec{a}_x + y\vec{a}_y + z\vec{a}_z$

The above equation represents a wave traveling in the +k-direction. We'll have opportunity to look at 3-D problems later.

# Exponential representation

Usually, if a cosine is a wavefunction of a particular wave equation, then the sine will also be a solution. A more general form of the wave function would be

$$f(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

However, we'll see that it is sometimes (in fact, often) more convenient to combine these terms into an exponential form:

$$f(x, t) = C \exp[i(kx - \omega t)]$$

where  $C$  is a complex coefficient. The exponential form contains all the information provided in the longer sinusoidal form given above. Again,  $f$  represents a wave traveling in the  $+x$  direction.

$$f(x, t) = D \exp[-i(kx - \omega t)]$$

represents a wave traveling the  $-x$  direction.

Lastly, we note that  $E = h\nu = h\frac{\omega}{2\pi}$

We will use this so much that we'll get tired of writing the extra  $2\pi$ , and so we define a "reduced Planck's constant":

$$\hbar = \frac{h}{2\pi}$$

$$E = \hbar\omega$$

Also, momentum has a very nice form when expressed in terms of  $k$ :

$$p = \frac{h}{\lambda} = \frac{h}{\frac{2\pi}{k}} = \frac{hk}{2\pi} = \hbar k$$

(  $\vec{p} = \hbar\vec{k}$  in three dimensions.)

Now we can think about extracting quantities of interest from the wave functions.

Starting with the simple exponential wave function, we can generate expressions for  $E$  and  $p$  using derivatives or “operators”.

Use the wave function for travel in the  $+x$  direction

$$\Psi(x, t) = C \exp [i (kx - \omega t)]$$

Taking the time derivative

$$\frac{\partial \Psi}{\partial t} = -i\omega C \exp [i (kx - \omega t)]$$

Multiplying by  $i\hbar$

$$\begin{aligned} i\hbar \frac{\partial \Psi}{\partial t} &= \hbar\omega C \exp [i (kx - \omega t)] \\ &= E\Psi \end{aligned}$$

Interesting: Taking the time derivative of the wave function and then multiplying by  $i\hbar$  gives the energy multiplied by the wave function.

The mathematical action (taking the time derivative and multiplying by  $i\hbar$ ) is called an *operator*. This particular one is called the *energy operator*.

$$i\hbar \frac{\partial}{\partial t} \rightarrow \text{energy operator}$$

When using an operator on a function results in a constant multiplying the original function, the function is known as an *eigenfunction* and the constant is known as an *eigenvalue*. (Eigen is German for “special”.) In the case the constant value would be known as the *eigenenergy*.

Operators play a central role in the mathematics of quantum mechanics. However, don't get too hung up on operators — the math is nothing new.



In similar fashion we can operate on the wave function with a spatial derivative

$$\frac{\partial \Psi}{\partial x} = ikC \exp [i (kx - \omega t)]$$

Multiplying by  $-i\hbar$

$$\begin{aligned} -i\hbar \frac{\partial \Psi}{\partial x} &= \hbar k C \exp [i (kx - \omega t)] \\ &= p \Psi \end{aligned}$$

$-i\hbar \frac{\partial}{\partial x} \rightarrow$  momentum operator.

So,  $\Psi$  is an also eigenfunction of the momentum operator with corresponding eigenvalue  $p$  (eigenmomentum).

We will make use of other operators as we move ahead in our understanding of QM.

To denote an operator mathematically, we put a little “hat” on it. For example, we could denote the momentum operator as

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

Using this notation in eigenfunction-eigenvalue expression:

$$\hat{p}\Psi = p\Psi$$

This is very compact, but would look sort of silly if you forgot the hat on the operator part.

# The crucial step

From classical physics, a *free* particle has only kinetic energy

$$E = K = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

Taking this as a hint of how to proceed with the wave picture, we can build a wave equation. Energy (apply the energy operator once) is equal to momentum squared (apply the momentum operator twice) divided by  $2m$ . Doing that:

$$\hat{E}\Psi = \frac{\hat{p}^2\Psi}{2m}$$

$$i\hbar\frac{\partial\Psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2}$$

We've defined a wave equation. Given the way that we constructed it, we already know that the solution is:

$$\Psi(x, t) = C \exp[i(kx - \omega t)]$$

(Try it — insert the solution back into the wave equation above.)

# The last piece

Now take the final step. From classical physics, the total energy of a particle is the sum of the kinetic and potential energies. In building up to the wave equation on the previous slide, we have used operators to give us the total energy and the kinetic energy (through the momentum operator). What about potential?

$$E = K + U = \frac{p^2}{2m} + U$$

Schroedinger assumed that it too must be an operator, and made a guess as to its form: He assumed that the potential energy operator is simply the potential energy function multiplied by the wavefunction.

$$\hat{U}\Psi \rightarrow U \cdot \Psi$$

Then the Schroedinger equation takes the form

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

To solve a particular quantum mechanics problem, we must find the appropriate potential energy, insert it into the Schroedinger equation, and work to find a solution. The solution will be the wave function, along with the corresponding energy and momentum. Note that we won't always care about all the pieces. Sometimes we need the wave function and other times just the energy may be sufficient.

As we discussed previously, the wave function tells us about the probability of finding the particle in a particular place and time. According to Born

$$\Psi^*(x, t) \Psi(x, t) \rightarrow \textit{probability density function}$$

$$\Psi^*(x, t) \Psi(x, t) dx \rightarrow \textit{probability of finding the particle between } x \textit{ and } x+dx$$

$$\int_{x_2}^{x_1} \Psi^*(x, t) \Psi(x, t) dx \rightarrow \textit{probability of finding the particle between } x_1 \textit{ and } x_2$$

We should be able to find the particle somewhere, which leads to the *normalization condition*.

$$\int_{-\infty}^{\infty} \Psi^* (x, t) \Psi (x, t) dx = 1$$

We can use the normalization condition to determine the undefined constants that always come with a solution to wave equations (eg. the factor  $C$  in the earlier plane waves.)

A wave function whose constants have been adjusted to meet the above condition is said to be *normalized*.

In looking at the probability equations above, note that the units of  $\Psi$  must be  $m^{-1/2}$ .

## Also note

Any real wave function must be finite and single-valued (i.e. it must be a “good” function).

And, it must be continuous and the first derivative must be continuous. (If not, there are real problems with the momentum of the particle.)

Defining the Hamiltonian operator

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

$$i\hbar \frac{\partial \Psi(x, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + U(x, t) \right] \Psi(x, t)$$

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

# Three-dimensional Schroedinger equation

In classical physics, the momentum is a vector and so has components in all three dimensions. We can define corresponding momentum operators for the three directions.

$$\hat{p}_x = -i\hbar \frac{\partial}{\partial x} \vec{a}_x \quad \hat{p}_y = -i\hbar \frac{\partial}{\partial y} \vec{a}_y \quad \hat{p}_z = -i\hbar \frac{\partial}{\partial z} \vec{a}_z$$

We can use the gradient operator to put all vector components in a compact form:

$$\hat{p} = -i\hbar \vec{\nabla} = -i\hbar \left[ \frac{\partial}{\partial x} \vec{a}_x + \frac{\partial}{\partial y} \vec{a}_y + \frac{\partial}{\partial z} \vec{a}_z \right]$$

Then, to define the kinetic energy (which requires using the momentum operator twice), we use the Laplacian:

$$\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2 = -\frac{\hbar^2}{2m} \left[ \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \right]$$

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