An Approach to the Schrödinger Equation

Classical Mechanics: Energy Conservation:

$$E = \frac{mv^2}{2} + V = \frac{p^2}{2m} + V \qquad with \qquad p = mv$$

Quantum physics: particles have wavelength and angular frequency:

$$\mathrm{p} = \frac{\mathrm{h}}{\lambda} \qquad \mathrm{E}_{\mathrm{kin}} = \hbar\omega \qquad \hbar = \frac{\mathrm{h}}{2\pi} \qquad \omega = 2\pi \mathrm{f}$$

A deBroglie particle-wave:

$$\Psi = A\exp\left[i\left(\frac{2\pi}{\lambda}x - \omega t\right)\right] = A\exp\left[\frac{i}{\hbar}\left(px - E_{kin}t\right)\right]$$

Here **E_{kin} is the kinetic energy** of the moving particle!

Quantum Mechanics: The Schrödinger Equation

Differentiating the particle wave equation twice with respect to x leads to

$$\frac{d^2}{dx^2}\Psi = -\frac{p^2}{\hbar^2}\Psi$$

Differentiating it once with respect to t and replacing E_{kin} with E from classical mechanics leads to

$$\frac{d}{dt}\Psi = -\frac{i}{\hbar}E\Psi = -\frac{i}{\hbar}\left(\frac{p^2}{2m} + V\right)\Psi$$

This is a generalization since the E_{kin} in the deBroglie wave is actually just the kinetic energy. We are looking for an equation that is also true for particles in a potential so we replaced the kinetic energy with the total energy. Generalizations like this lead to a new theory which cannot be derived from any other theory. It is not possible to derive a theory, one can only develop it. One theory never follows from another. If it did it wouldn't be a theory.
From the two last equations we can construct a differential equation as follows:
We multiply the first by $-\hbar^2/2m$ and the second by $i\hbar$ to give:

$$-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\Psi = \frac{p^2}{2m}\Psi$$

And

$$i\hbar\frac{d}{dt}\Psi = \left(\frac{p^2}{2m} + V\right)\Psi$$

If we add $V\Psi$ to the first of these equations the right hand sides are identical so the left hand sides should be too and we get a differential equation from the left hand sides.

$$i\hbar\frac{d}{dt}\Psi = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]\Psi$$

This is the **time-dependent Schroedinger equation in one dimension**. It can be generalized to three dimensions with the abbreviation

$$\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$$

To give the **time-dependent Schroedinger equation**.

$$i\hbar\frac{d}{dt}\Psi = \left[-\frac{\hbar^2}{2m}\nabla^2 + V\right]\Psi$$

The expression in brackets is called the **Hamilton operator *H*** (it performs a mathematical operation on Ψ).

$$i\hbar\frac{d}{dt}\Psi = H\Psi$$

Ψ is called the **wave function**. It is a complex valued function of x, y, z and t. The wave function has no physical interpretation but its **absolute square $|\Psi|^2$** is understood as the **probability** to find the particle inside a small volume at position x, y, z and time t, devided by the size of this volume. This is a **probability density**.

If a particle is bound in a potential, for example an electron bound in an atom, the probability density does not depend on time, The probability to find a particle in a certain volume in a certain position is always the same. The orbital does not change shape.

A wave function with a time-independent probability density can be constructed as follows:

$$\Psi(x, y, z, t) = \exp\left(-i\frac{E}{\hbar}t\right)\psi(x, y, z)$$

with an absolute square that depends only on x,y and z and not on time since

$$|\Psi|^2 = \Psi\,\Psi^* = \exp\left(-i\frac{E}{\hbar}t\right)\psi(x,y,z)\exp\left(i\frac{E}{\hbar}t\right)\psi^*(x,y,z) = \psi\,\psi^* = |\psi|^2$$

We'll insert this wave function into the time-dependent Schrödinger equation now but we will stick to the one-dimensional case

$$\Psi(x,t) = \exp\left(-i\frac{E}{\hbar}t\right)\psi(x)$$

to give:

$$i\hbar\frac{d}{dt}\left[\exp\left(-i\frac{E}{\hbar}t\right)\psi(x)\right] = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]\left[\exp\left(-i\frac{E}{\hbar}t\right)\psi(x)\right]$$

The differentiation with respect to t on the left can be carried out directly, wheras on the right the exponential can be moved in front of the bracket since it only depends on t and not on x.

$$i\hbar\left(-i\frac{E}{\hbar}\right)\exp\left(-i\frac{E}{\hbar}t\right)\psi(x) = \exp\left(-i\frac{E}{\hbar}t\right)\left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]\psi(x)$$

which simplifies to

$$E\psi(x) = \left[-\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V\right]\psi(x)$$

or swapping right and left side, using *H* for the Hamilton operator and generalizing to three dimensions

$$H\,\psi(x,y,z) = E\,\psi(x,y,z)$$

This is the **time-independent Schrödinger equation** which describes orbitals that are constant in time.