VI. TIME INDEPENDENT SCHRÖDINGER EQUATION

The usual situation for quantum particles is in some kind of a confining potential. When this is the case, it is not so easy to discuss the wave function as a combination of plane waves, and rely on our perfect intuition from Fourier transforms. One must approach the Schrödinger equation with the respect it deserves as a partial differential equation.

One way in which we can solve partial differential equations is by separation of variables. By this we mean the following. Instead of thinking of the wave function, $\psi(x,t)$, as a combination of waves, we will make a guess commonly refered to as separation of variables:

$$\psi(x,t) = T(t)\psi(x) \tag{110}$$

So we are going to assume that solutions of the equation can be written as a product of two independent functions that depend on x and t separately.

Let's see how this works in the context of the Schrdinger equation:

$$i\hbar\psi(x)\frac{\partial T(t)}{\partial t} = -\left[\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)\right]T(t) \tag{111}$$

The RHS depends only on $T(t)$ itself, untouched by the derivatives. Same for the LHS an $\psi(x)$. Therefore we can write:

$$i\hbar\frac{1}{T(t)}\frac{\partial T(t)}{\partial t} = \left[-\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)\right]\frac{1}{\psi(x)} \tag{112}$$

Now, the RHS depends only on x, so it must be independent of time. The LHS depends only on t, so it must be independent of x. So if we take the separation of variables ansatz seriously, we must accept that:

$$\begin{gathered} i\hbar\tfrac{1}{T(t)}\tfrac{\partial T(t)}{\partial t} = E \\ = \left[-\tfrac{\hbar^2}{2m}\tfrac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x)\right]\tfrac{1}{\psi(x)} \end{gathered} \tag{113}$$

with E a constant. We then need to first solve:

$$i\hbar\frac{\partial T(t)}{\partial t} = ET(t) \tag{114}$$

Which is easily done:

$$T(t) = e^{-itE/\hbar} \tag{115}$$

This brings about an easy interpretation of the parameter E - the energy. comparing this with the wave solution we get:

$$E = \hbar\omega \tag{116}$$

aha - the Planck relationship.

This comparison with the energy is further supported by the second equation that we must solve:

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} + V(x)\psi(x) \tag{117}$$

This is the time-independent Schrödinger equation.

The TISE is a second order differential equation (don't let the partial derivative confuse you - there is no time appearing anywhere!). Naively, it looks as if every value of E should produce two solutions: right moving and left moving. This is true in free space - $e^{\pm ikx}$ but not when a potential, or, alternatively, boundary conditions, are present. Then it turns out that only a limited values of solutions exists. Let us demonstrate this on the simplest problem in the book - the particle in a box.

A. Particle in a box

Ultimately, we would like to speak about a cat in a box. But we must build up to it. So let's think of a single particle - an atom, or an electron - in a box. It is convenient to think of the box as located in the range:

$$0 < x < L \tag{118}$$

The particle can be inside the box with no problem: $V(x) = 0$ inside. But outside is forbidden - to leave the box the particle must overcome insurmountable walls. What should we take for the potential? $V(x) = \infty$ outside:

$$v(x) = \begin{cases} 0 & 0 < x < L \\ \infty & x \leq 0, x \geq L \end{cases} \tag{119}$$

But if the particle can not be outside the box, what is its wave function outside the box? zero. In particular,

$$\psi(0) = \psi(L) = 0. \tag{120}$$

This should be true independent of time. Eq. (120) together with the TISE:

$$E\psi(x) = -\frac{\hbar^2}{2m}\frac{\partial^2\psi(x)}{\partial x^2} \tag{121}$$

in the range $0 < x < L$ [which reflects $V(x)$ being given by Eq. (119)] is the complete problem of a particle in a box.

We seem to have a time independent 2nd order free differnetial equation. What are its solutions ignoring the boundary condition? Usually I advocate that you get used to thinking of complex exponentials as solutions for wave equations, or equations like this one:

$$\psi(x) = e^{\pm ikx} \tag{122}$$

which upon substitution in the equation give:

$$k = \frac{\sqrt{2mE}}{\hbar}. \tag{123}$$

Today, however, I'm going to be more traditional, and accept your tendency to think in terms of trigonometric functions. We want a function that will be zero at $x = 0$. What is a good candidate that combines the two waves above?

$$\psi(x) = A\sin(kx) \tag{124}$$

with k still obeying the relation (123). Cosine will never do, since it doesn't vanish at $x = 0$. This is not sufficient yet. We have another boundary condition: $\psi(L) = 0$. This requires:

$$\psi(L) = A\sin(kL) = 0 \tag{125}$$

Which requires:

$$k = k_n = \frac{\pi}{L}n. \tag{126}$$

But now we can look back and see that indeed not all energies are possible. Only:

$$E_n = \frac{(\hbar k_n)^2}{2m} = \frac{\hbar^2\pi^2}{2mL^2}n^2. \tag{127}$$

B. small distraction: Bohr-Sommerfeld quantization

Let's take a small historical detour. This result was essentially guessed by Niels Bohr and Arnold Sommerfeld, when the former condidered the quantization of levels in an atom.

Before De-Broglie waves were known or understood, they came up with the following idea, roughly. In a closed classical orbit, the action should be quantized. What is the action?

$$S = \int \vec{p} \cdot \vec{d\ell} \tag{128}$$

The integral along the path of the momentum dot the displacement. This should be a quantity that looks like another familiar quantity - the work along a path. The quantization rule is:

$$\int \vec{p} \cdot \vec{d\ell} = 2\pi\hbar n \tag{129}$$

They basically guessed it since the action has the same dimensions as the Planck constant.

Let's see if it works for the particle in a box. What is the closed classical orbit? Going to the right with momentum p and then returning with the same momentum, but with opposite direction. Therefore:

$$\int \vec{p} \cdot \vec{d\ell} = 2pL = 2\pi\hbar n \tag{130}$$

Indeed:

$$k_n = \frac{\pi}{L} n \tag{131}$$

We can see how this quantization rule agrees with the idea of de-Borglie waves. If we think about a wave function that goes through a non-uniform medium, it makes sense to generalize the wave function to:

$$\exp(ipx/\hbar) \to \exp(i \int^x dx \vec{p} \cdot \vec{d\ell}/\hbar) \tag{132}$$

And then we see that the accumulated phase of the wave as it moves, is just the action along the path.