A PRIMER ON THE QUANTUM MECHANICS OF POTENTIAL WELLS

Wave Function

The wave function ψ for a quantum system contains all the information that you can ever know about that system. The energy, momentum, spin and any other physical quantity can be obtained using the wave function. If a wave function describes a particle, then the probability of finding the particle in a particular place is determined by the square of the amplitude of the wave function at that point.

Technically speaking, the probability of finding a particle between position x and position $x + dx$ is given by:

$$P(x) = |\psi(x)|^2 = \psi(x)^*\psi(x).$$

You can only have one probability for finding a particle at a particular location, so the wave function must be a single-valued function. As a consequence, if you move between two different zones in which the wave function is of different shape or form, the wave function has to be continuous at the boundary between them.

Time-Independent Schrödinger Equation

If you are interested in the energy of a quantum mechanical system, one way or another you solve the Time-Independent Schrödinger equation (TISE). This can be written:

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

The operators in the square brackets represent kinetic and potential energy. The eigenvalues of this equation E give the values of total energy that the system can exist in. In many systems where a particle is confined to a region of space by a force that generates a potential well, these are restricted to particular values, giving rise to energy levels. In one-dimension, the TISE reduces to:

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

Two Simple Examples

A particle moves in a region of space with a constant potential V_0 and positive kinetic energy. This situation is classically allowed as the total energy E is greater than the potential energy, i.e. $E - V_0$ is a positive number. The TISE for this case is written:

$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V_0\right]\psi(x) = E\psi(x).$$

Rearranging:
$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = (E - V_0)\,\psi(x).$$
Writing $k^2 = 2m\,(E - V_0)\,/\hbar^2$ gives:
$$\frac{d^2\psi(x)}{dx^2} = -k^2\psi(x).$$
The solution is a function that differentiated twice gives the original function multiplied by a negative number, i.e. $\psi(x) = A\sin kx + B\cos kx$. The constants A and B need to be determined by the boundary conditions of the region and by the need to make sure that probabilities add up to unity.

A particle moves in a region of space with a constant potential V_0 and negative kinetic energy. This situation is classically forbidden as the total energy E is less than the potential energy, i.e. $E - V_0$ is a negative number. For example, a ball will only run up a hill, losing kinetic energy and gaining potential energy, until the kinetic energy falls to zero. Classically, it cannot move further up the hill; if it did it would have a negative value of kinetic energy. However, in quantum mechanics the uncertainty principle allows the borrowing of some energy, for a period of time, which would allow the particle to roll a little further into the classically forbidden region. The TISE has the uncertainty principle built into it. The TISE is again:
$$\left[\frac{-\hbar^2}{2m}\frac{d^2}{dx^2} + V_0\right]\psi(x) = E\psi(x).$$
Rearranging:
$$\frac{-\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} = (E - V_0)\,\psi(x).$$
But let's make it clear that $E - V_0$ is less than zero by writing it as $-|E - V_0|$. Again $k^2 = 2m|E - V_0|/\hbar^2$ now gives:
$$\frac{d^2\psi(x)}{dx^2} = k^2\psi(x).$$
The solution is function that differentiated twice just gives the original function multiplied by a positive number, i.e. $\psi(x) = Ce^{kx} + De^{-kx}$. Usually C has to be set to zero; if not ψ becomes infinite and we cannot then arrange for the sum of all probabilities to be equal to one, a process called normalisation of the wave function. Hence $\psi(x) = De^{-kx}$ representing the fact that there is a small probability of being in this classically forbidden region, but the probability of doing so falls off exponentially the deeper you go into the forbidden zone.

De Broglie's Hypothesis

De Broglie considered the wave-like properties of particles moving in free space and decided their wavelength λ would be related to their momentum p by the relationship $\lambda = \frac{h}{p}$ where h is Planck's constant. Particles moving in free space would be the first situation that we analysed above so their wave function would be $\psi(x) = A \sin kx + B \cos kx$ where $p = \hbar k$.

Given de Broglie's relationship, it should be clear that the smaller the wavelength of the wave function, the higher the particle's momentum is and therefore the higher it's energy.

Strictly speaking, this only applies to free particles, cases where the potential is a constant. Under these conditions the wave function is harmonic and the wavelength is a constant. This is analogous to waves moving along a Slinky, for example. When the potential is not a constant, the wave functions are not harmonic functions, and wavelength is not a well defined quantity. (A classical example might be a heavy chain held at one end and dangling down, the tension changes along the length due to the weight of the links. Waving the end results in what looks like a wave, but with a wavelength that changes down the chain.) However, in some cases, often the wave functions look a little bit like a particular sine or cosine and one can loosely speak of a wavelength (or technically speaking a Fourier analysis might indicate the harmonic decomposition is dominated by one harmonic function). In these cases, you can get a strong feeling for the energy of the state guided by de Broglie's relationship.

Quantum Mechanical of Potential Wells

A potential well is just a set of zones of different potential energy, e.g. a finite well is just two regions of high potential with a zone of lower potential between them. Classically, a particle would be trapped in the potential well if it's energy was smaller than the depth of the well. Quantum mechanically, we've seen that a particle can exist in a classically forbidden region, so we'd expect the probability of finding the particle in the well to be high, but a small probability of finding it outside that diminishes rapidly the further we are away from the well.

Mathematically, the way to find the wave function in this case is to solve the TISE in each region, then match the solutions at the boundary between them. This means making sure that the wave function is continuous (i.e. single-valued) at the interfaces, but also that it doesn't have any kinks by making the slope of the wave function continuous also.

Often a useful intuitive way to think about it is to consider that you are fitting standing waves into the potential well. Consider an *infinite square well* as a simple case. Notice that outside the well $V_0 = \infty$, and the only way to satisfy the TISE is to make $\psi = 0$ outside. In this particular case, we have a region with zero probability of finding the particle i.e. classically and quantum mechanically forbidden. So at the boundary we have to make $\psi = 0$. Inside the potential is constant, so inside the wave function has to be harmonic. We can match these to the outside by having harmonic standing waves inside which have nodes at the edge of the well (see diagram). The wavelengths then have to satisfy the condition $n\frac{\lambda}{2} = a$, where n is an integer and a is the width of the square well.

In this case, the wave functions are perfectly harmonic, wavelength is perfectly well defined and you can use de Broglie to calculate the energy of each standing wave, assuming we choose the definition of potential to be zero inside the well:

$$E = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} = \frac{n^2h^2}{8ma^2}.$$

So we've ended up with a series of discrete energy levels for different values of the integer n, which correspond to wave functions with different wavelengths. If you just try to solve the TISE directly, then match the solutions, this is exactly what you get.

Notice that the energies increase if the well shrinks. You're reducing the wavelengths and so increasing momentum and energy.

An infinite square well is not exactly physically reasonable. Usually they have finite well depths, so we have to consider the solution of a *finite square well* in most realistic cases. We'll do the maths in the lecture, but think about this intuitively. If the bottom of the well is flat, and the sides vertical, then there are two zones, inside and outside. If the particle sits in the well, its energy will be less than the top. Inside the potential is constant i.e. harmonic wave function. Outside it is a classically forbidden region, the wave function will be exponentially falling. We then need to match a harmonic function onto these decaying exponentials. The shorter the wavelength of the harmonic part, the higher the energy is. So we have guessed what the solution to this problem looks like, despite the mathematics being more complicated!