

5.2: States of Definite Energy

Separation of Variables

Now that we have the Schrödinger equation, we can link the physical circumstances the particle finds itself in to its wave function, and from that we can make probabilistic predictions of its behavior. So now our attention turns to actually *solving* this differential equation. Like the classical wave equation before it, the Schrödinger equation in one dimension (which we will focus on for quite awhile) is a partial differential equation with two variables. As we did with string waves all the way back in [Section 1.2](#), we will start by looking only at a certain family of solutions to this differential equations – those that can be separated into a product of two functions of single variables. While to this point we have used the symbol ψ for both the time-dependent wave function $\psi(x, t)$ and the wave form $\psi(x)$, from this point on to avoid confusion, we will use the capitalized version Ψ for the time-dependent wave function $\Psi(x, t)$ and retain the lower-case ψ for the time-independent version.

Following the separation method we used before, we write the full wave function as the product of two others:

$$\Psi(x, t) = \psi(x) \cdot \tau(t) \quad (5.2.1)$$

This time we plug it into the Schrödinger equation:

$$\begin{aligned} -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \Psi(x, t) + V(x) \Psi(x, t) &= i\hbar \frac{\partial}{\partial t} \Psi(x, t) \Rightarrow -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} [\psi(x) \cdot \tau(t)] + V(x) [\psi(x) \cdot \tau(t)] \\ &= i\hbar \frac{\partial}{\partial t} [\psi(x) \cdot \tau(t)] \end{aligned} \quad (5.2.2)$$

The partial derivatives only act on the function of the same variable, so representing derivatives of the single variable in each case with primes, we have:

$$-\frac{\hbar^2}{2m} \psi''(x) \tau(t) + V(x) \psi(x) \tau(t) = i\hbar \psi(x) \tau'(t) \quad (5.2.3)$$

Dividing both sides of the equation by $\psi(x) \tau(t)$ gives:

$$\frac{-\frac{\hbar^2}{2m} \psi''(x) + V(x) \psi(x)}{\psi(x)} = i\hbar \frac{\tau'(t)}{\tau(t)} \quad (5.2.4)$$

The left side of this equation is exclusively a function of x , while the right side is exclusively a function of t . For these to be equal for all values of x and t , they must equal a common constant, and that gives us two ordinary (single variable) differential equations that share a common constant. Before we continue with the math, we should think about what physical quantity this constant might be. When we derived the Schrödinger equation, we noted that the first term links the wave function to the particle's kinetic energy, and of course the second term links it to the potential energy. Given that this sum will equal a constant multiplied by the wave function, it seems reasonable to conclude that the constant is the total energy, E . This also works with the right side of the equation, given the relationship we have seen for the time portion of the plane wave:

$$\frac{-\frac{\hbar^2}{2m} \psi''(x) + V(x) \psi(x)}{\psi(x)} = E = i\hbar \frac{\tau'(t)}{\tau(t)} \quad (5.2.5)$$

$$\Rightarrow -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \psi(x) + V(x) \psi(x) = E \psi(x), \quad i\hbar \frac{d}{dt} \tau(t) = E \tau(t) \quad (5.2.6)$$

The time-independent wave function that satisfies the first differential equation depends upon the specifics of $V(x)$ (and of course boundary conditions), but the form of the solution to the second differential equation (absent of an initial condition) looks like:

$$\tau(t) = \tau_0 e^{-i\omega t}, \quad \text{where: } \omega \equiv \frac{E}{\hbar} \quad (5.2.7)$$

Ultimately we will use the functions $\psi(x)$ and $\tau(t)$ to rebuild $\Psi(x, t)$, and of course $\Psi(x, t)$ will need to be normalized in order for the probability density derived from it to give proper results. The probability density will then be:

$$\mathcal{P}(x, t) = |\Psi(x, t)|^2 = \psi^*(x) \tau^*(t) \psi(x) \tau(t) = |\psi(x)|^2 |\tau_0|^2 e^{+i\omega t} e^{-i\omega t} = |\tau_0|^2 |\psi(x)|^2 \quad (5.2.8)$$

It will be easier for us later if we insist that the time-independent wave function $\psi(x)$ itself be normalized, and with the total probability density also normalized, we choose the simplification that $\tau_0 = 1$, and the time portion of our separated wave function is simply equal to $e^{-i\omega t}$.

Special Physical Conditions

There are two special physical (measurable) conditions that accompany these separable solutions to the Schrödinger equation. The first we can see from the previous equation, which (with our choice of τ_o) reduces to simply:

$$\mathcal{P}(x, t) = |\psi(x)|^2 \quad (5.2.9)$$

This shows that in fact the probability density does not change with time. Physically this means that it when we compute the probability of finding the particle at a specific location, that probability doesn't change with time. We have seen this many times already – for example, the probability of a particle landing at a specific position on a screen after passing through a double-slit does not fluctuate with time. For this reason, we call such solutions the *stationary-state* solutions to Schrödinger's equation – the quantum state remains unchanging ("stationary") in time. It should be emphasized that the wave function itself is changing with the passage of time – its quantum phase is oscillating with frequency ω . But as we have discussed previously, the wave function does not determine probabilities directly – only its *magnitude-squared* has any significance (it is the probability density), and for these separated wave functions the time part of the wave function – while it exists – does not contribute.

The second physical condition that accompanies this type of solution to the Schrödinger equation is the energy. As we know, whenever we measure a quantity for a quantum state, in general that quantity can take on several values. A wave packet has many measurable positions and momenta, for example. But with a single energy emerging from the separation of variables, we see that measurement of the energy of a particle described by such wave function can only yield a single value.

So stationary quantum states are states of definite energy. It is useful to introduce language that we will use frequently from now on. We say that the energy associated with one of these wave functions is the *eigenvalue* of energy ("eigen" is German for "own" - this is the value of energy "owned" by this state). Such a state is also referred to as an *eigenstate* of energy. Plane wave states (which have single values of momentum) are eigenstates of momentum and, as it happens, of energy as well, since they have a fixed kinetic energy and no potential energy. It is therefore not surprising that plane wave functions are separable.

Building General Wave Functions

When we first used separation of variables, we found that the separated single-variable functions were harmonic, and that these solutions could be combined together in a Fourier series to construct any periodic function. If the potential energy of the particle is zero (i.e. it is free), then the separated functions are also harmonic (plane waves), and those too can be combined to make more general free particle states (wave packets). Well it turns out that even more generally, separated solutions to the Schrödinger equation with a potential energy can also be put together to construct any general state subject to that potential *even though the separated solutions are not strictly harmonic* when the potential is not zero (or a constant). This fact is the statement of what is called the *spectral theorem*, but it is well beyond the scope of this course to go any further than to state this as fact. The technical language you will hear in this regard is, "the collection of the stationary state solutions for the Schrödinger equation with a given potential energy forms a complete set of states". *Completeness* refers to the fact that all of the possible solutions can be constructed in this way.

Another way to think of this is once again in terms of vectors. The three unit vectors \hat{i} , \hat{j} , and \hat{k} are "complete" in that any 3-dimensional vector can be formed from a linear combination of these. So the various separable solutions form a (typically infinite) set of orthogonal functions, linear combinations of which can be constructed to build any general solution.

It's important to understand that when using multiple stationary state solutions of the Schrödinger equation to build a more general solution, the result is *not* a stationary state solution. When we used two plane waves to construct another solution to the free particle Schrödinger equation, we did not get back another plane wave solution (we can't put together two harmonic waves with different wavelengths to get a new harmonic wave with a new wavelength!). To see this explicitly, let's consider two stationary-state solutions $\Psi_1(x, t)$ and $\Psi_2(x, t)$, associated with energies E_1 and E_2 . If we create a new solution (which in this case is not normalized, but we'll come back to that issue later) by mixing these in equal amounts, we get:

$$\begin{aligned} \Psi_{tot}(x, t) &= \Psi_1(x, t) + \Psi_2(x, t) = \psi_1(x) e^{-i\omega_1 t} + \psi_2(x) e^{-i\omega_2 t} \\ \Rightarrow \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \Psi_{tot}(x, t) &= \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi_1(x) e^{-i\omega_1 t} + \left[-\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x) \right] \psi_2(x) e^{-i\omega_2 t} \\ &= E_1 \psi_1(x) e^{-i\omega_1 t} + E_2 \psi_2(x) e^{-i\omega_2 t} \end{aligned} \quad (5.2.10)$$

Clearly this does not have the form of a stationary state solution, as the functions of time cannot be made to go away.

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