

The Schrödinger Equation

1 Equation of Motion for Wave-Particle Duality

In light of the de Broglie hypothesis, the interference pattern of electrons through a double slit, the diffraction of electrons through a single slit, and other supporting evidence, we have to now think of particles as possessing a wave aspect. This raises a problem, however: As we said in the discussion of the uncertainty principle, it is not possible to say that a wave is located at a specific location. Since a particle has a wavelength, therefore, we cannot specify exactly where it is. The best we can do is say that a particle is “approximately here”. To put this more precisely, the best we can do is to specify the region of space where it could be: For example, we might say that the particle is contained within the volume of space \mathbb{V} bounded¹ by $\langle x, y, z \rangle$ and $\langle x + dx, y + dy, z + dz \rangle$.

Is that all we need? No, for the next question automatically is, “*where* in that region is the particle?”. Again, though, it is not possible to *calculate* an answer to that question. We must perform a *physical measurement*. However, we can think about it this way:

We know that, although we cannot predict (calculate) *exactly* where the particle is in \mathbb{V} , it is certainly in there *somewhere*. Thus, if I actually go to the trouble of doing an experiment to measure the location of the particle, the position I get is guaranteed to be somewhere in the volume \mathbb{V} . Furthermore, it is at least plausible to think that not all locations in \mathbb{V} are equally likely; although it is in there somewhere, it is *more likely* to be in some places than in others. Next, we have to assume that those probabilities change as time goes on.

So where does this leave us? Well, recall Newton’s 2nd law:

$$\frac{d^2x}{dt^2} = \left(\frac{1}{m}\right) \left(-\frac{dV}{dx}\right) \quad (1)$$

The canonical problem in *classical* mechanics is that we have a (classical) particle of mass m subject to a force² F , and we want to be able to calculate (predict) where it will be at any time. Once we specify the potential energy function $V(x)$, we have a second-order differential equation; solving it means to obtain the function $x(t)$. This

¹In some cases, the “boundary” may be the ends of the universe, i.e., $\mathbb{V} = \mathbb{R}^3$

²Remember that $F = -\frac{dV}{dx}$.

function allows us to predict what the the position x of the particle will be at time t . We have the option of checking this prediction, but we know that if we do everything competently, our experimental result will match our calculation—with 100% certainty.

Notice that all of this is possible because, classically, we consider a particle to a solid object with a definite location. I could reasonably refer to Eq. 1 as “the particle function”.³

In *quantum* mechanics, instead, we are limited to trying to find a function that will tell us the *probability* that a particle will be at a particular location at a particular time. Thus, we want to obtain a function that allows us to calculate not x , but rather the *probability* that the particle will be at x (at some time t). In contrast with the classical result, *we cannot know where the particle actually is until we measure it*. This is, again, because the “particle” has a wavelength, and thus is spread out inside \mathbb{V} . The function we attempt to find, then, is reasonably referred to as “the wave function”, and it is given the symbol Ψ . It is, as mentioned above, a function of both position and of time, so $\Psi = \Psi(x, t)$.

1.1 The Statistical Interpretation

The conceptual problem is that a particle, by its nature, is localized at a point, whereas the wave function Ψ is spread out in space (it’s a function of x). How can such a function be said to describe the state of a particle? The answer is provided by Born’s **statistical interpretation** of the wave function which says that $|\Psi(x, t)|^2$ gives the *probability of finding the particle at a point x , at a time t* —or, more precisely,

$$|\Psi(x, t)|^2 dx = \text{the probability of finding the particle between } x \text{ and } (x + dx), \text{ at time } t.$$

So, a large value of $|\Psi|^2$ indicates a large probability of finding the particle in the vicinity of x , and a small value indicates a small probability.

The statistical interpretation introduces a kind of indeterminacy into quantum mechanics, for even if you know everything the theory has to tell you about the particle (to wit: its wave function), you still cannot predict with certainty the outcome of a single experiment to measure its position—all quantum mechanics has to offer is statistical information about the possible results.

Until 1964, there were three major schools of thought on how to interpret this fact. In that year, however, the American physicist John Bell showed⁴ that one of the interpretations—the so-called “Copenhagen interpretation”—was correct:⁵

³No one ever does use this name; I made it up to highlight what is coming next.

⁴Exactly *how* he showed this is a fascinating story that, alas, I cannot go into here. (If you are interested, look up “Bell’s inequality”.)

⁵It is called this because it was developed by a group of the leading physicists of the day, at a meeting that took place in (surprise) Copenhagen, Denmark.

Suppose I *do* measure the position of the particle, and I find it to be at the point X_0 . **Question:** Where was the particle just *before* I made the measurement? **Answer:** *The particle wasn't really anywhere.* It was the act of measurement that forced the particle to “choose” X_0 (though how and why it “decided” on the point X_0 we dare not ask). One physicist put it this way: “Observations not only *disturb* what is to be measured, they *produce* it... We *compel* the particle to assume a definite position.” A particle simply does not *have* a precise position prior to measurement; it is the measurement process itself that insists on one particular number, and thereby in a sense *creates* the specific result, limited only by the statistical weighting imposed by the wave function.

But what if I made a *second* measurement, immediately after the first? Would I get X_0 again, or does the act of measurement cough up some completely new number each time? On this question, at least, everyone is in agreement: A repeated measurement (on the same particle) must return the *same* value. Evidently the first measurement radically alters the wave function, so that it is now sharply peaked about X_0 .⁶ There are, then, two entirely distinct kinds of physical processes: “ordinary” ones, in which the wave function evolves in a leisurely fashion dictated by the Schrödinger equation, and “measurements”, in which Ψ suddenly and discontinuously “collapses”.⁷

2 Schrodinger's Equation

Recall that the general form for a standing wave is

$$\Psi(x,t) = \psi(x) f(t) \quad (2)$$

Notice that ψ (lower case) is a function of position only, and f is a function of t alone. (Solutions of the wave equation that take this form, where the x -dependence and the t -dependence are separate are known, reasonably enough, as **separable solutions**.) Now, the wave equation is not the only differential equation that gives us physically interesting information. Thus, for mysterious reasons of my own, let's find the the solutions to the following equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi \quad (3)$$

This equation is known as the **Schrödinger equation**; like the wave function (which it superficially resembles), its solution $\Psi(x,t)$ tells us the behavior (motion as a function

⁶ Ψ soon spreads out again, in accordance with the Schrödinger equation, so the second measurement must be made quickly.

⁷The role of measurement in quantum mechanics is so critical and so bizarre that you may well be wondering what precisely *constitutes* a measurement. Does it have to do with the interaction between a microscopic (quantum) system and a macroscopic (classical) measuring apparatus (as Bohr insisted), or is it characterized by the leaving of a permanent “record” (as Heisenberg claimed), or does it involve the intervention of a conscious “observer” (as Wigner proposed)? We will take the naive view: A measurement is the kind of thing that a scientist does in the laboratory, with rulers, stopwatches, Geiger counters, and so on.

of space and of time) of a particle of mass m ; the major difference is that, in this case, we include the fact that the particle is subject to a potential energy function $V(x)$ that is a function of x only; it is independent of time. (Recall that the force on an object is the derivative of the potential energy function: $F = -\frac{dV}{dx}$.)

2.1 Schrodinger's Equation in 3d

In three dimensions, the time-dependent Schrodinger equation reads (in operator form)

$$H\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (4)$$

The operator H is obtained from

$$\frac{\mathbf{p}^2}{2m} + V = \frac{1}{2m} (p_x^2 + p_y^2 + p_z^2) + V$$

where, remember, \mathbf{p} is the momentum operator⁸:

$$p_x = \frac{\hbar}{i} \frac{\partial}{\partial x}, p_y = \frac{\hbar}{i} \frac{\partial}{\partial y}, p_z = \frac{\hbar}{i} \frac{\partial}{\partial z}$$

or, more simply,

$$\mathbf{p} = \frac{\hbar}{i} \nabla \quad (5)$$

Thus, Schrodinger's equation in three dimensions can be written

$$-\frac{\hbar^2}{2m} \nabla^2 \Psi + V\Psi = i\hbar \frac{\partial \Psi}{\partial t} \quad (6)$$

The potential energy V and the wave function Ψ are now functions of $\mathbf{r} = (x, y, z)$, and Ψ is also⁹ a function of t . The probability of finding the particle in a differential-sized volume element d^3r is $|\Psi(\mathbf{r}, t)|^2 d^3r$, and the wave functions must be normalized:

$$|\Psi(\mathbf{r}, t)|^2 d^3r = 1 \quad (7)$$

where this volume integral is over all space. Since we are restricting our attention to potentials that are independent of time, then the solutions to Schrodinger's equation

⁸Up to now, I have been indicating that a particular quantity is an operator by putting a "hat" on it, to distinguish it from the corresponding observable. The hats will become very cumbersome soon, and there won't be much chance of confusion from here on out, so I am going to leave them off from now on.

⁹ V is still independent of time.

(for a given potential function $V(\mathbf{r})$) will form a complete set of functions in Hilbert space:

$$\Psi_n(\mathbf{r}, t) = \psi_n(\mathbf{r}) e^{-i \frac{E_n t}{\hbar}} \quad (8)$$

where the spatial part of the wave function satisfies

$$-\frac{\hbar^2}{2m} \nabla^2 \psi_n + V \psi_n = E_n \psi_n \quad (9)$$

The general solution to the time-dependent Schrodinger equation is therefore

$$\Psi(\mathbf{r}, t) = \sum_n c_n \psi_n(\mathbf{r}) e^{-i \frac{E_n t}{\hbar}} \quad (10)$$

with the constants c_n determined by the initial wave function $\Psi(\mathbf{r}, 0)$ by applying the initial conditions in the usual way.

Notice that Equations 6 through 10, unchanged, allow for *any* coordinate system you choose to use.

3 Separation of Variables

Let's get expressions for the left and right sides of Equation 3. The left hand side is

$$\frac{\partial \Psi}{\partial t} = \psi \frac{df}{dt}$$

and the right-hand side is

$$\frac{\partial^2 \Psi}{\partial x^2} = \frac{d^2 \psi}{dx^2} f$$

(ordinary derivatives, now), and so the Schrödinger equation reads

$$i\hbar \psi \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{d^2 \psi}{dx^2} f + V \psi f$$

Dividing through by ψf (which, remember, are both functions) gives

$$i\hbar \frac{1}{f} \frac{df}{dt} = -\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2 \psi}{dx^2} + V$$

Now the left side is a function of t alone, and the right side is a function of x alone.¹⁰ The only way this equation can possibly be true is if both sides are in fact *constant*—otherwise, by varying t , I could change the left side without changing the right side, and the two sides would no longer be equal. (This is a subtle, but crucial argument, so if it's new to you, be sure to pause and think it through.) For reasons that will appear later, we shall call this constant E . Then,

$$i\hbar \frac{1}{f} \frac{df}{dt} = E \quad (11)$$

or

$$\frac{df}{dt} = -\frac{iE}{\hbar} f \quad (12)$$

for the left side, and

$$-\frac{\hbar^2}{2m} \frac{1}{\psi} \frac{d^2\psi}{dx^2} + V = E \quad (13)$$

or

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\psi = E\psi \quad (14)$$

for the right side. This mathematical approach, which is called **separation of variables**, has turned one *partial* differential equation (which is very hard to solve) into two *ordinary* differential equations, each of which is (comparatively) easy to solve. For Eq. 12, we just multiply through by dt , divide by f , and integrate; the general solution is $Ce^{-\frac{iE}{\hbar}t}$, but we may as well absorb the constant C into ψ [since the quantity of interest is ultimately $\psi(x)f(t)$]; then

$$f(t) = e^{-\frac{iE}{\hbar}t} \quad (15)$$

The second equation above, Eq. 14, is called the **time-independent Schrödinger equation**; we can go no further with it until the potential $V(x)$ is specified.

4 Solving Schrodinger's Equation

What I want to do next is solve the Schrödinger equation, and interpreting the solution physically. As I said earlier, we need to specify the potential for a particular system in order to come up with a specific solution for our system. (This is reasonable, since the potential energy function $V(x)$ gives us the force $F = -\frac{dV}{dx}$, which gives us acceleration, velocity, momentum, energy, and so on.) Thus, I will choose several important potential energy functions, substitute them into Schrodinger's equation, and solve them. Each different $V(x)$ will produce a different differential equation, and thus they will have to be solved by different methods.

¹⁰Notice this would *not* be true if V were a function of t as well as of x .