MATH 404: Introduction to Partial Differential Equations
Term Paper
The Schrödinger Equation

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1 Historical Background

Since the experiments of Huygens and Young in the 18th and 19th centuries, it had been firmly established that light exhibits certain wave-like properties [see any general source, such as Burdge and Overby (2015), for an overview of the details in this introduction]. Maxwell in 1864 discovered that electromagnetic waves propagate at the speed of light. The quantum hypothesis of Planck (1900) proposed that photons can only be emitted in certain discrete energy levels (or *quanta*), which were found to be proportinal to a new constant $h = 6.626 \times 10^{-34} J \cdot s$. In 1905, Einstein explained the photoelectric effect by hypothesizing that, beyond simply being *emitted* or *absorbed* in certain energy levels, light itself light itself was actually constrained to *exist* in those discrete levels, with the energy proportional to the frequency, $E = h\nu$. Bohr (1912) applied this insight to successfully model the hydrogen atom by assuming that its *electrons* were constrained to certain energy levels, or shells. Finally, de Broglie (1926) interpreted matter as a wave whose momentum was proportional to its wavelength, $p = \frac{h}{\lambda}$.

Two remarkable things about all these models stand out: first, they revealed that quantities which under the classical framework were assumed able to take on a continuous range of values were instead limited to coming in specific "bits" or "quanta". Second, properties like momentum and energy were suddenly shown to depend on wave properties such as wavelength and frequency.

Taken together, these two facts suggest that an accurate description of the new "quanta" and their behavior should model wave behavior that depends on discrete energy states. In modeling real behavior, the goal is to get a description of the phenomena being studied that doesn't contradict any other known facts and explains as much of what is known to occur as possible. So we need to take a description of reality that models wave behavior (developed from mathematical theory) and try to incorporate the "quantized" matter-energy relations

known to work experimentally.

2 Deriving the Equation

Start with the one-dimensional classical wave equation, $u_{tt} = c^2 u_{xx}$. This has the general (wave train) solution $u(x,t) = Ae^{i(kx-\omega t)}$, where k is the wavenumber and ω is the angular frequency. As long as the amplitude is a constant, we can leave it aside to be dealt with after we have the solution, so let the wave function $\Psi(x,t) = e^{i(kx-\omega t)}$.

But how do we get from the abstract mathematics of the wave equation to a description of reality? The above-mentioned relations between energy, momentum, and wave parameters discovered by Einstein and de Broglie provide the link between the equation and the real objects it is to describe.

From Einstein, we have $E = h\nu$, where E is energy in joules, ν is the linear frequency (s^{-1}) and Planck's constant $h = 6.626 \times 10^{-34}\ J \cdot s$. For a wave, the linear frequency $\nu = \frac{\omega}{2\pi}$, allowing us to express this relation in terms of angular frequency: $E = \frac{h\omega}{2\pi}$. As a matter of convenience, we define the "reduced" Planck's constant $\hbar = \frac{h}{2\pi}$ so that we can write energy solely in terms of angular frequency as $E = \hbar\omega$. Therefore $\omega = \frac{E}{\hbar}$.

From de Broglie, $\lambda = \frac{h}{p}$, where λ is wavelength ($meters$) and p is momentum $\left(kg \cdot \frac{m^2}{s^2}\right)$, in SI units. Here we use the relation for wavenumber $k = \frac{2\pi}{\lambda}$, giving $k = \frac{p}{\hbar}$.

There is one more quantity that must be rewritten. In the one-dimensional wave equation $u_{tt} = c^2 u_{xx}$, the wave speed c is equal to the (linear) frequency multiplied by the wavelength, or $c = \lambda\nu$. With $k = \frac{2\pi}{\lambda}$, this yields $c = \frac{2\pi\nu}{k}$.

But now we have a conundrum: "energy" as an abstract concept is fine for philosophers, but for real applications it has a specific form (or multiple forms) which it has to be expressed in if we want to use our quantum-wave equation to solve physical problems. For physical systems, the total energy E is a sum of the kinetic energy T and the potential energy V, $E = T + V$. Potential is usually given by some known function $V(x,t)$ - in an experiment, we might be supplying some electromagnetic potential of known magnitude and mathematical representation. But kinetic energy depends on more basic physical parameters, mass and velocity. These need to be incorporated to replace the abstract T with something we can actually use.

In the classical (non-relativistic) case, momentum $p = mv$. We can use this to rewrite the kinetic energy $T = \frac{1}{2}mv^2$ as $T = \frac{p^2}{2m}$. Then the total energy is given by $E = \frac{p^2}{2m} + V$. Next we use the relations above to express momentum in terms of wave properties: $p^2 = 2m\,(E - V) = \frac{h^2}{\lambda^2}$.

Finally, on to the actual equation! We obtain here only the time-independent form of the Schrödinger equation, as it is simpler and can be derived using only the wave equation and the wave-property relations developed above (Sherrill, 2001b). Time-independence, in the language of PDEs, indicates that the equation does not depend on derivatives of time. This suggests we need to eliminate the time-derivative somehow. We will use the *ansatz* that Ψ can be separated into $\Psi(x,t) = X(x)T(t)$, and substitute this into the standard wave equation to solve by separation of variables. [This derivation is based on the treatments of Sherrill (2001a) and Ward and Volkmer (2006)]

We need a form of T(t) that will lend itself to elimination of the t variable, leaving an equation only in x. Use the temporal part of the wave train solution, $e^{-i\omega t}$. Substitute:

$\Psi_{tt} = c^2\Psi_{xx},\ \Psi(x,t) = X(x)T(t) \rightarrow XT'' = c^2X''T$. We want to keep the x-derivatives, so let $X'' = \frac{X}{c^2}\frac{T''}{T}$.

Now $T(t) = e^{-i\omega t},$ so $T''(t) = -\omega^2 e^{-i\omega t},$ and $\frac{T''}{T} = -\omega^2$.

We now have $\frac{\partial^2 X}{\partial x^2} = -\frac{\omega^2}{c^2}X$, satisfying the criterion for a PDE with derivatives only in x. To incorporate the physical parameters, we use $c = \frac{2\pi\nu}{k}$, $\omega = 2\pi\nu$ to rewrite

$\frac{\omega^2}{c^2} = k^2\frac{\cancel{(2\pi\nu)^2}}{\cancel{(2\pi\nu)^2}}$

From above, $k^2 = \frac{p^2}{\hbar^2},$ and with

$p^2 = 2m\,(E - V)\,,$ we have (finally)

$\frac{\partial^2 X}{\partial x^2} = -\left[\frac{2m(E-V)}{\hbar^2}\right]X$

Which, conventionally written

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

is the time-independent Schrödinger equation in one variable. Here the notation $X(x)$ is usually replaced by a lowercase ψ to indicate that the spatial part of the wavefunction is being operated on:

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

The derivation of the more complicated (and more general) time-dependent form is not dealt with here. The two forms differ in their derivation; while the time-independent equation can be derived as above, "the time-dependent Schrödinger equation cannot be derived using elementary methods." (Sherrill, 2001b) To ensure that the eigenvalues are real (see the end of section 3), only the time-independent equation will be examined in this paper.

3 Intuitions about a Solution

By the probabilistic (Born) interpretation, the square of a system's wavefunction for a given state corresponds to the probability of finding the system in that state (Fitzpatrick 2013). For a system that actually exists (i.e., a physical situation being modeled), the probability of finding the system in one of the possible states must be 100%. For a continuous (non-discrete) set of possible states, this means

$$\int |\psi|^2 = 1$$

since integration is really just an infinite summation (ibid).

But what if the integral isn't equal to 1? When we have a problem whose solution must give a known output, we can (and must, if we want to solve the problem) *construct* the data used in the problem so that it gives the required outcome. If we know the integral has to equal 1, then as long as the integral is convergent, the integrand can be modified by a constant to give the required total probability. (This is the approach known as *normalization*: Suppose $\int |\psi|^2 = C$, where C is a constant. Multiply ψ by another constant D such that $\frac{C}{D^2} = 1$. Then $\int |\Psi|^2 = 1$.) (ibid)

The requirement that $\int |\psi|^2$ be definite immediately identifies all valid wavefunctions ψ as members of L^2

space. This gives us an error check: if the wavefunction we find isn't square-integrable in both x and t, then it isn't a solution. (However, this applies only for particles in bound states; see Levine, p. 55).

Finally, note that the time-independent equation can be written in a form that satisfies the conditions of a regular Sturm-Liouville problem:

$$\begin{cases} \partial_x(p(x)u_x(x)) - q(x)u(x) = -\lambda\sigma(x)u \quad x \in (a,b) \\ \alpha u(0) + \beta u_x(0) = 0 \\ \gamma u(L) + \delta u_x(L) = 0 \end{cases}$$

If we redistribute the negative sign in the time-independent equation, we get:

$$\left\{ \frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} - V(x)\psi(x) = -E(x)\psi(x) \right.$$

and we can *construct* the boundary terms by the proper choice of problem (see section 4, below) so that

$$\begin{cases} \psi(0) = 0 \\ \psi(L) = 0 \end{cases}$$

Here, the terms in the PDE-boundary problem correspond to:

$$\begin{cases} p(x) = \frac{\hbar^2}{2m} \\ q(x) = V(x) \\ \lambda_n = E_n(x) \\ \sigma(x) = 1 \\ \alpha = 1 \\ \gamma = 1 \end{cases}$$

For a regular Sturm-Liouville problem, the following must hold (Webster 2017a):

(1) p, q, σ are continuous on (a,b) : **satisfied** as long as $V(x)$ is continuous on (a,b).

(2) p is continuously differentiable on (a,b) : **satisfied**.

(3) p and σ are strictly positive on (a,b) : **satisfied** (this was what required swapping the negative signs).

(4) q is nonnegative on (a,b) : **satisfied** as long as $V(x)$ is positive on (a,b).

(5) $\left(\alpha^2+\beta^2\right)$ and $\left(\gamma^2+\delta^2\right) \neq 0$: **satisfied** for $\alpha,\gamma = 1$.

Therefore the following are true (ibid):

- the eigenvalues are real, discrete, and ordered
- each eigenvalue is associated with a unique eigenfunction

These facts are of import because we want energy to be a real quantity, so we need to choose "well-posed" problems that will give us answers we can use. Like any tool, the Schrödinger equation only works when applied to what it was designed for. (An engineering student's insight).

4 Solving the Equation

To solve an equation that models a physical system, we need to know the physical parameters of that system. Quantum physics is concerned, foremost, with particles and their behavior around energy potentials.

4.1 The Time-Independent Equation: Particle in a Box

4.1.1 The Infinite Well

The classic "particle in a box" scenario envisions a potential well of specified value along two vertical lines and zero value along the x-axis connecting them. The idealized "infinite well" model is considered first.

Let the infinite "walls" of the well be at $x=0$ and $x=L$. Since this is a "rectangular" well, $V(x)$for $x<0=V(0)$ and $V(x), x>L=V(L)$, both $V(0)$ and $V(L)$ being infinite. The PDE then becomes:

$$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x) - V(x)\psi(x),\ V(x) = \begin{cases} 0 & 0<x<L \\ \infty & x<0, x>L \end{cases}$$

Treating x outside of $(0, L)$ first (for reasons that will become clear):

$-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x) - \lim_{y\to\infty} y\psi(x) \to -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = \psi(x)[E - \lim_{y\to\infty} y] \to \frac{-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x)}{[E - \lim_{y\to\infty} y]} = \psi(x) = 0.$ (following Levine, p. 23)

Clearly, an infinite well cannot be traversed by a wavefunction, so the particle is confined within the well. This might represent a situation where a particle is known to be within a certain area, with the boundaries of the area being modeled as infinite to give the desired result.

Within the well, $V(x) = 0$ and we have $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x),$ which is just a second-order ODE in x. Its characteristic polynomial gives roots $\pm i\frac{\sqrt{2mE}}{\hbar}$, with general solution

$$\psi(x) = A\sin\left(\frac{\sqrt{2mE}}{\hbar}x\right) + B\cos\left(\frac{\sqrt{2mE}}{\hbar}x\right).$$

But now we need boundary conditions. Wait! We know that $\psi = 0$ outside the well, and that sine and cosine are both L^2 functions on $(0, L)$. This *suggests* that the wavefunction should be continuous at the boundary between the different potential regions (see also Levine, p. 23, where the assumption derives from smoothness of the derivatives). So we now plug in the boundary conditions $\psi(0) = \psi(L) = 0$:

For $x = 0$ we find that $B = 0,$ and for $x = L$ we have eigenvalues $\frac{\sqrt{2mE}}{\hbar}L = n\pi.$

Solving for energy E gives

$$E = \frac{1}{2m}\left(\frac{\hbar n\pi}{L}\right)^2 \to E = \frac{1}{2m}\frac{\hbar^2 n^2\pi^2}{L^2} = \frac{1}{2m}\frac{\hbar^2 n^2 \cancel{\pi^2}}{4\cancel{\pi^2}L^2} = \frac{h^2 n^2}{8mL^2}.$$

And so we come to the essential fact of quantum theory: some physical quantities (in this case, energy) are constrained to only take on certain discrete values, and cannot vary over a continuous range.

Now let's examine the first three eigenfunctions, $s_1,$ $s_2,$ and s_3 (by evaluating the term inside sine and then considering its effect on $\psi(x)$) :

$s_1:\ \frac{1}{\hbar}\sqrt{\frac{2\cancel{m}h^2(1^2)}{8\cancel{m}L^2}} = \frac{2\pi}{h}\frac{h}{2L} = \frac{\pi}{L}.$
$s_2:\ \frac{1}{\hbar}\sqrt{\frac{2\cancel{m}h^2(2^2)}{8\cancel{m}L^2}} = \frac{2\pi}{h}\frac{h}{L} = \frac{2\pi}{L}.$

$s_3: \ \frac{1}{\hbar}\sqrt{\frac{2\cancel{m}\hbar^2(3^2)}{8\cancel{m}L^2}} = \frac{2\pi}{h}\frac{h}{L} = \frac{2\pi}{3L}.$

For s_1, we have a linear amplitude multiple of whose period $k = \frac{2\pi}{\frac{\pi}{L}} = 2L$. For any length L of our well, the particle will require $2L$ to complete one cycle. The wavefunction will take the form of the upper part of a sine graph.

s_2 has period $k = \frac{2\pi}{\frac{2\pi}{L}} = L$ or one complete cycle of the sine wave over the length L. There will be two "humps" to the wavefunction.

s_3, with period $3L$, will complete three cycles in twice L or one and a half cycles over L. There are three humps in the wavefunction, the ones on the end always opposite in amplitude to the center.

However, it is important to differentiate (in the non-mathematical sense!) between the form of the wavefunction and its interpretation as the probability density. The wavefunction equation plotted by itself will go below the line $V = 0$ for half of its cycle. But the location of the particle described by the wavefunction is given by the *square* of the wavefunction, so the particle will never be below the well.

This is a very simple example of the problem - more inherent, perhaps, in quantum mechanics than in any other field of knowledge ever devised - of determining what relation the model has to the thing being modeled.

What is striking is that, here, the energy does not depend on the amplitude of the wave. In the "classical" model of a plucked string, the initial profile (how far the string is stretched before release) represented the potential energy imparted to the string through tension, whose value determines the magnitude of the u_{xx} term.

Lastly, let's look at the problem using energy methods. Multiply through by ψ and integrate:

$-\frac{\hbar^2}{2m}\int_0^L \psi\psi_{xx}dx = \int_0^L E\psi^2 dx$

We can use the "grown-up way of thinking about integration by parts" (Webster 2017b) to rewrite the left-hand side:

$\int_0^L (\psi_x)^2\, dx + \left[\psi\psi_x\,|_0^L\right] = \frac{2m}{\hbar^2}\int_0^L E\psi^2 dx$

(where the negative sign was kept on the left so that it could cancel out the negative picked up when integrating by parts). Since $\psi = 0$ at the endpoints, the second term vanishes and we are left with $\int_0^L (\psi_x)^2 \, dx = \frac{2m}{\hbar^2} \int_0^L E\psi^2 dx$. As the integral of the first derivative squared, the left term can be considered analogous to the "potential energy" of the system. For all finite energies of the particle, then, the potential is a constant. The implication is that energy does not dissipate for the particle in an infinite potential well. (This is implied from the lack of a dispersive term in the PDE, but we have now proven it.)

4.1.2 The Finite Well

The finite well scenario has the walls of the potential well being of finite value. This might be thought of as trying to keep something penned in using walls of finite size, like a particle in an electromagnetic field (or an octopus in an aquarium tank). We're pretty sure we have it trapped, but the octopus might be crafty enough (or the particle "quantum-y" enough) to break out, because the walls don't strictly forbid it.

For simplicity the potential is assumed to be a "flat" potential

$$V(x) = \begin{cases} 0 & 0 < x < L \\ V_0 & x < 0, x > L \end{cases}$$

yielding the PDE

$$\begin{cases} E\psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) & 0 < x < L \\ E\psi(x) = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \psi(x) + V_0 \psi(x) & x < 0, x > L \end{cases}$$

Now the PDE has a finite term modifying the energy: $\psi_{xx} + \frac{2m}{\hbar^2}(E - V_0)\psi = 0$. Allowing the potential to be finite has changed the nature of the solutions. In addition, we now have to consider the parts of the x-axis beyond $(0, L)$, since there is no infinite potential there to cancel out the value of ψ.

For $x \in (0, L)$ note that since the PDE is the same as before, **if** the initial/boundary data is the same, then by uniqueness of solutions the wavefunction will be the same. (No boundary data is given in this scenario, so we will not assume this.)

The cases considered are then $E > V_0$ and $E < V_0$. Note that E cannot equal V_0 (Irvine, p. 29; Landau and

Lifshitz, pp. 63-65) because then $(E - V_0) = 0,$ giving $\psi = 0$ for $E \neq 0,$ which gives us the absurd situation of a particle that is nowhere but has finite energy!

$E > V_0$

Here the coefficient of the $\psi(x)$ term is positive: $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = (E - V_0)\psi(x) \rightarrow \frac{\partial^2}{\partial x^2}\psi(x) + \frac{2m}{\hbar}(E - V_0)\psi(x) = 0.$ The roots are complex and the general solution given by

$$\psi(x) = A\sin\left(\sqrt{\tfrac{2m}{\hbar}(E - V_0)}x\right) + B\cos\left(\sqrt{\tfrac{2m}{\hbar}(E - V_0)}x\right)$$

$E < V_0$

The characteristic equation now has real coefficients, and

$$\psi(x) = C\exp\left(\sqrt{\tfrac{2m}{\hbar}|E - V_0|}x\right) + D\exp\left(-\sqrt{\tfrac{2m}{\hbar}|E - V_0|}x\right) \text{ (note the absolute value of } (E - V_0))$$

In order to have a solution which exists for $E < V_0,$ we need $\psi(x)$ to be finite. This indicates, following Landau and Lifshitz (p. 64), that $C = 0$ for $x > 0$ (so that the D term is finite) and $D = 0$ for $x < 0$ (so the same happens for the C term). For $x \in (0, L)$ we would ordinarily have both parts. But wait! Energy can't be negative, and on $(0, L)$, $V_0 = 0,$ ruling out any solution on $E < V_0,$ $0 \leq x \leq L.$ We see that the particle cannot be inside the well when $E < V_0$:

$$\begin{cases} \psi(x) = C\exp\left(\sqrt{\tfrac{2m}{\hbar}|E - V_0|}x\right) & E < V_0, x < 0 \\ \psi(x) = D\exp\left(-\sqrt{\tfrac{2m}{\hbar}|E - V_0|}x\right) & E < V_0, x > L \end{cases}$$

For $E > V_0,$ the solution $\psi(x) = A\sin\left(\sqrt{\tfrac{2m}{\hbar}(E - V_0)}x\right) + B\cos\left(\sqrt{\tfrac{2m}{\hbar}(E - V_0)}x\right)$ is constrained to be finite, meaning that $\lim_{x\to\pm\infty}\psi(x)$ must vanish. This constrains solutions for $E > V_0$ to exist inside the well. (see Cumalat (2013), slide 22).

Putting it all together:

$$\begin{cases} \psi(x) = C\exp\left(\sqrt{\frac{2m}{\hbar}|E-V_0|}x\right) & E < V_0, x < 0 \\ \psi(x) = D\exp\left(-\sqrt{\frac{2m}{\hbar}|E-V_0|}x\right) & E < V_0, x > L \\ \psi(x) = A\sin\left(\sqrt{\frac{2m}{\hbar}(E-V_0)}x\right) + B\cos\left(\sqrt{\frac{2m}{\hbar}(E-V_0)}x\right) & E > V_0, 0 < x < L \\ \psi(x \searrow 0) = \psi(x \nearrow 0) \\ \psi(x \searrow L) = \psi(x \nearrow L) \end{cases}$$

What to make of this? It says that the particle can have less total energy than potential energy, and can be found outside of the well even if it begins within it (Cumalat, slide 22). The two different areas are known as the **bound** and **unbound** states (Irvine, p. 30). In classical physics, we would not be able to have $T < 0$ because it would imply that velocity is imaginary. "Velocity", however, turns out to be a somewhat different thing in the quantum world. (It is not even clear that it is defined here). In additon, the "classical" behavior (Cumalat, slide 22) we are accustomed to has given way to the possibility of finding that the particle has suddenly "jumped" across the well, the phenomenon called **tunneling** (Irvine, p. 30) which also has no analog in our classical world.

We required, in setting up this problem, that there be a nonzero probability of finding the particle outside the well, but in working through the problem with that assumption we let quantum mechanics show its weirdness once again in an entirely unexpected way.

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