# PHY 115A
# Lecture Notes:
# Time-Independent Schrödinger Equation
# (Griffith's Chapter 2)

Michael Mulhearn

October 2, 2023

# Chapter 2

# Time-Independent Schrödinger Equation

## 2.1 Stationary States

Here's our summary of Griffiths section 2.1:

We attempt to solve the Schrödinger Equation:

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\,\Psi \tag{2.1}$$

in the case that the potential V(x) is not a function of $t$. We will try to find a solution under the assumption that $\Psi(x,t)$ is separable:

$$\Psi(x,t) = \psi(x)\,\phi(t) \tag{2.2}$$

which yields:

$$\begin{aligned} i\hbar\,\psi \frac{d\phi}{dt} &= -\frac{\hbar^2}{2m}\,\phi \frac{d^2\psi}{dx^2} + V\,\Psi \\ i\hbar\,\frac{1}{\phi(t)} \frac{d\phi}{dt} &= -\frac{\hbar^2}{2m}\,\frac{1}{\psi(x)} \frac{d^2\psi}{dx^2} + V(x) \end{aligned}$$

As the LHS is a function of $t$ only, and the RHS a function of $x$ only, both sides must be constant wrt $t$ and $x$ respectively. We'll call that constant $E$, and solve for $\phi(t)$:

$$\begin{aligned} i\hbar\,\frac{1}{\phi(t)} \frac{d\phi}{dt} &= E \\ \int \frac{d\phi}{\phi(t)} &= -\frac{iE}{\hbar} \int dt \\ \ln \phi &= -\frac{iEt}{\hbar} \\ \phi(t) &= \exp(-\frac{iEt}{\hbar}) \end{aligned}$$

The remaining equation is for $\psi(x)$ only

$$-\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + V\,\psi = E\psi$$

and is called the Time-Independent Schrödinger Equation (TISE), often just called the Schrödinger Equation when the meaning is clear.

In classical mechanics, the total energy (kinetic plus potential) is called the Hamiltonian:

$$H(x,p) = \frac{p^2}{2m} + V(x)$$

We can construct the corresponding operator in quantum mechanics by substituting

$$\begin{aligned} x &\rightarrow \hat{x} = x \\ p &\rightarrow \hat{p} = -i\hbar\frac{\partial}{\partial x} \end{aligned}$$

to calculate:

$$\hat{H} = H(\hat{x},\hat{p}) = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) \tag{2.3}$$

with which we can write the TISE as:

$$\hat{H}\,\psi(x) = E\,\psi(x) \tag{2.4}$$

We'll demonstrate later the following boundary conditions on $\psi(x)$:

- $\psi(x)$ is always continuous.
- $d\psi/dx$ is continuous except where the potential is infinite.

Note that these conditions do not apply to $\Psi(x,t)$ no $\partial\Psi/\partial x$ which need not be continuous. Some observations left as exercises (See Griffith's problems 2.1 and 2.2)

- For normalizable solutions, we must the separation constant E real.
- $\psi(x)$ can always be taken real.
- If $V(x)$ is an even function, than $\psi(x)$ can be taken as even or odd.
- $E$ must be greater than the minimum value of $V(x)$.

The separable solutions are important solutions because:

- They represent **stationary states**: even though the "full" wave function

  $$\Psi(x,t) = \phi(t)\,\psi(x) = e^{-iEt/h}\,\psi(x)$$

  has a time dependence, the probability density is constant with time:

  $$\begin{aligned} |\Psi(x,t)|^2 &= \left(e^{-iEt/h}\,\psi(x)\right)^*\,\left(e^{-iEt/h}\,\psi(x)\right) \\ &= e^{iEt/h-iEt/h}\,\psi^*(x)\psi(x) \\ &= |\psi(x)|^2 \end{aligned}$$

  This means that every expectation value is constant wrt time as well. It also follows that:

  $$\int_{-\infty}^{+\infty} |\psi(x)|^2 dx = 1$$

- They represent **states of definite total energy:** the expectation value for the total energy of a separable solution is:

$$\begin{aligned}\langle E\rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t)\,\hat{H}\,\Psi(x,t)\;dx \\ &= \int_{-\infty}^{+\infty} \psi^*(x)\,\hat{H}\,\psi(x)\;dx \\ &= \int_{-\infty}^{+\infty} \psi^*(x)\,E\,\psi(x)\;dx \\ &= E\int_{-\infty}^{+\infty} |\psi(x)|\;dx \\ &= E\end{aligned}$$

  Remember that we just chose $E$ as the symbol for the constant value when using separation of variables. This shows why we choose $E$, as that constant is the expectation value of the total energy. Now calculate in a similar fashion:

$$\begin{aligned}\langle E^2\rangle &= \int_{-\infty}^{+\infty} \Psi^*(x)\,\hat{H}^2\,\Psi(x)\;dx \\ &= E^2\end{aligned}$$

  From which it follows:

$$\sigma_H^2 = \langle<\rangle\, E^2 > - \langle E\rangle^2 = E^2 - E^2 = 0$$

  This means that every measurement of the particles total energy will yield the result $E$.

- There is more, but (unlike Griffiths) we will leave those features for later.

## 2.2 Infinite Square Well

Next we will turn our attention to the infinite square well:

$$V(x) = \begin{cases} 0 & 0 \le x \le a \\ +\infty & \text{otherwise} \end{cases} \tag{2.5}$$

By setting $V(x) = +\infty$ outside the well, we just mean $\Psi(x,t) = 0$ in that region, and not anything more. We also see that for normalizable solutions, we must have $E > 0$.

We are looking for the stationary states that solve the TISE:

$$\hat{H}\,\psi(x) = E\,\psi(x)$$

Inside the well we have:

$$\begin{aligned}-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} &= E\,\psi(x) \\ \frac{d^2\psi}{dx^2} &= -k^2\psi\end{aligned}$$

where

$$k \equiv \frac{\sqrt{2mE}}{\hbar}$$

Taking $\psi(x)$ to be real, the solutions are:

$$\psi(x) = A\sin(kx) + B\cos(ks)$$

And the continuity requirements on $\psi(x)$ imply:

$$\psi(0) = \psi(a) = 0.$$

Why is there no continuity condition on $d\psi/dx$? Applying the conditions:

$$\psi(0) = A\sin(0) + B\cos(0) = B = 0$$

So now:

$$\psi(x) = A\sin(kx)$$

And applying the other condition:

$$\begin{aligned} \psi(a) &= A\sin(ka) = 0 \\ \sin(ka) &= 0 \end{aligned}$$

Where in the last step we have used $A \neq 0$ because $A = 0$ implies $\psi(x) = 0$ a non-normalizable solution. The sin function is zero for any integer value of pi, so:

$$\begin{aligned} ka &= n\pi \\ k_n &= \frac{n\pi}{a} \end{aligned}$$

where $n$ is any integer. The normalization condition implies:

$$\begin{aligned} \int_{-\infty}^{+\infty} |\psi(x)|^2\,dx &= 1 \\ 1 &= \int_0^a |A\,\sin(k_n x)|^2\,dx \\ 1 &= |A|^2 \int_0^a \sin(k_n x)|^2\,dx \\ 1 &= |A|^2\,\frac{a}{2} \\ |A|^2 &= \frac{2}{a} \end{aligned}$$

As the phase of $A$ doesn't matter for the purposes of normalization, we choose it to be positive real

$$\begin{aligned} \int_{-\infty}^{+\infty} |\psi(x)|^2\,dx &= 1 \\ A &= \sqrt{\frac{2}{a}} \end{aligned}$$

So at last we have an infinite number of solutions to the TISE:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin(k_n x) \tag{2.6}$$

where

$$k_n = \frac{n\pi}{a}$$

In principle, $n$ can be any integer, but for $n = 0$ we get the unnormalizable wave function $\psi(x) = 0$ and so we omit $n = 0$. We note also that:

$$\psi_{-n}(x) = \sqrt{\frac{2}{a}}\sin(k_{-n}x) = \sqrt{\frac{2}{a}}\sin(-k_n x) = -\sqrt{\frac{2}{a}}\sin(k_n x) = -\psi_n(x)$$

So $\psi_{-n}$ differs from $\psi_n$ only by a phase factor $-1$ and therefore adds nothing (recall that we simply chose $A$ to be positive and real). So we can omit negative values of $n$ as well. That leaves us with:

$$n = 1, 2, 3, \ldots$$

Recalling our definition for $k$, the definite total energy $E_n$ of stationary state $\psi_n$ is given by:

$$\begin{aligned} k_n &= \frac{n\pi}{a} = \frac{\sqrt{2mE_n}}{\hbar} \\ E_n &= \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \end{aligned}$$

You may recognize the $\psi_n(x)$ as ...

## 2.3 The Fourier Series as a Vector Space

In this section, we'll see how the Fourier Series defines a Vector Space.

We'll start by definining the properties of a vector space in the familiar setting of the 3-D Euclidean Vectors.

### 2.3.1 Euclidean Vector Space

We are going to be introducing the concept of a vector space, so let's review this in the context of ordinary euclidean vectors in three dimensional space. Such a vector is completely specified by its displacement in each spatial direction. Let's look at this familiar picture a bit formally, to prepare us to apply it in a less intuitive (but mathematically equivalent) setting.

We have **vector addition** with the following properties:

- **Closure under addition:** The addition of two vectors is another vector:

$$\vec{u} + \vec{v} = \vec{w}$$

- **Commutative**:

$$\vec{u} + \vec{v} = \vec{v} + \vec{u}$$

- **Associated**:
$$\vec{u} + (\vec{v} + \vec{w}) = (\vec{u} + \vec{v}) + \vec{w}$$

- **Zero**: There is the vector 0 with:
$$\vec{u} + 0 = \vec{u}$$

- **Inverse vector**: For every $\vec{u}$ there is $(-\vec{u})$ s.t.:
$$\vec{u} + (-\vec{u}) = 0$$

We have **scalar multiplication** with the following properties:

- **Closure under scalar multiplication:** The product of a scalar and a vector is another vector:
$$a\vec{u} = \vec{w}$$

- **Distributive**:
$$a(\vec{u} + \vec{v}) = a\vec{u} + a\vec{v}$$

- **Associative**:
$$a(b\vec{u}) = (ab)\vec{u})$$

- **Multiplication by one**:
$$1\vec{u}) = \vec{u}$$

- **Multiplication by zero**:
$$0\vec{u}) = 0$$

We also have the dot product, but this is called an **inner product** within an $n - dimensional$ vector space:
$$\vec{v} \cdot \vec{w} = v_x w_x + v_y w_y + v_z w_z$$
You already know how to do this for ordinary vectors. In other settings, we use the more general term *inner product*. To describe any vector we need a set of *basis vectors*, in this case $\hat{x}$, $\hat{y}$, and $\hat{z}$. These basis vectors are orthogonal:
$$\hat{x} \cdot \hat{y} = \hat{y} \cdot \hat{z} = \hat{z} \cdot \hat{x} = 0$$
and normalized:
$$\hat{x} \cdot \hat{x} = \hat{y} \cdot \hat{y} = \hat{z} \cdot \hat{z} = 1.$$
When the basis vectors have both of these properties, we call them *orthonormal*.

For any possible vector $\vec{v}$, we can calculate its component in the direction of each basis vector by calculating the inner product:
$$v_x = \vec{v} \cdot \hat{x}$$
$$v_y = \vec{v} \cdot \hat{y}$$
$$v_z = \vec{v} \cdot \hat{z}$$

We say that the basis vectors $\hat{x}$, $\hat{y}$, and $\hat{z}$ are "complete", because specifying the values of $v_x$, $v_y$, and $v_z$ completely describes the vector $v$. The set of basis vectors $\hat{x}$ and $\hat{z}$ are orthonormal, but they are not complete in three dimensional space, because there are vectors which we cannot write using only these two directions. For instance, there are no possible values for $v_x$ and $v_z$ which make

$$\vec{v_1} = v_x\hat{x} + v_z\hat{z}$$

equal to the vector

$$\vec{v_2} = 3\hat{x} + 2\hat{y} + 7\hat{z}.$$

Orthogonality and completeness are intimately related. In Euclidean vector space, any three orthogonal vectors must be complete.

## 2.4 The Fourier Series

Using the language of vector spaces, the Fourier Theorem states that the sines and cosines form a complete orthonormal basis for any periodic function.

The vectors in this vector space are periodic functions. Vector addition of the vectors $f(x)$ and $g(x)$ is just $f(x)+g(x)$ which is another vector. Scalar multiplication is just multiplying a function $f(x)$ by a scalar $a$ to get a new function $af(x)$. The other properties of vector addition and scalar multiplication easily follow from the corresponding rules of ordinary addition and multiplication.

We need to define the inner product. If we restrict ourselves to real functions of $x$ with period $a$, the inner product between any two functions $f(x)$ and $g(x)$ is defined to be the integral:

$$\langle f|g\rangle \equiv \int_{-\frac{a}{2}}^{\frac{a}{2}} f(x)g(x)\,dx \tag{2.7}$$

The basis vectors are the sine and cosine functions

$$s_n(x) \equiv \sqrt{\frac{2}{L}}\sin\left(\frac{2\pi n}{L}x\right) \tag{2.8}$$

$$c_n(x) \equiv \sqrt{\frac{2}{L}}\cos\left(\frac{2\pi n}{L}x\right) \tag{2.9}$$

which are defined for

$$n = 0, 1, 2, 3, ... \tag{2.10}$$

We'll leave it as an exercise to show that:

$$\langle s_n|s_m\rangle = \frac{2}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} \sin\left(\frac{2\pi n}{L}x\right)\sin\left(\frac{2\pi m}{L}x\right)dx = \delta_{nm} \tag{2.11}$$

$$\langle c_n|c_m\rangle = \frac{2}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} \cos\left(\frac{2\pi n}{L}x\right)\cos\left(\frac{2\pi m}{L}x\right)dx = \delta_{nm} \tag{2.12}$$

$$\langle s_n|c_m\rangle = \frac{2}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} \sin\left(\frac{2\pi n}{L}x\right)\cos\left(\frac{2\pi m}{L}x\right)dx = 0 \tag{2.13}$$

where for compact notation we will use the Kronecker delta symbol:

$$\delta_{nm} = \begin{cases} 1 & \text{if } n = m \\ 0 & \text{otherwise} \end{cases}$$

Last of all, they are *complete* because any periodic function with period $L$ can be written as a sum of these sines and cosines:

$$f(x) = \sqrt{\frac{2}{L}} \sum_{n=0}^{\infty} A_n \cos\left(\frac{2\pi n}{L} x\right) + \sqrt{\frac{2}{L}} \sum_{n=1}^{\infty} B_n \sin\left(\frac{2\pi n}{L} x\right) \tag{2.14}$$

The values $A_n$ and $B_n$ are called *Fourier coefficients*. Technically the $N$th term in the Fourier Series refers to the approximation for $f(x)$ from the first $N$ terms in the infinite sum above, and we say that the Fourier Series converges to the function $f(x)$. Note that $s_0(x) = 0$, which is why the second sum begins at $n = 1$. The demonstration of completeness is optional reading, available in the Appendix.

For a visual example of the Fourier Series, the first terms of the Fourier Series for a step function are shown in Fig. A.1.

## 2.5 Determining the Fourier Coefficients

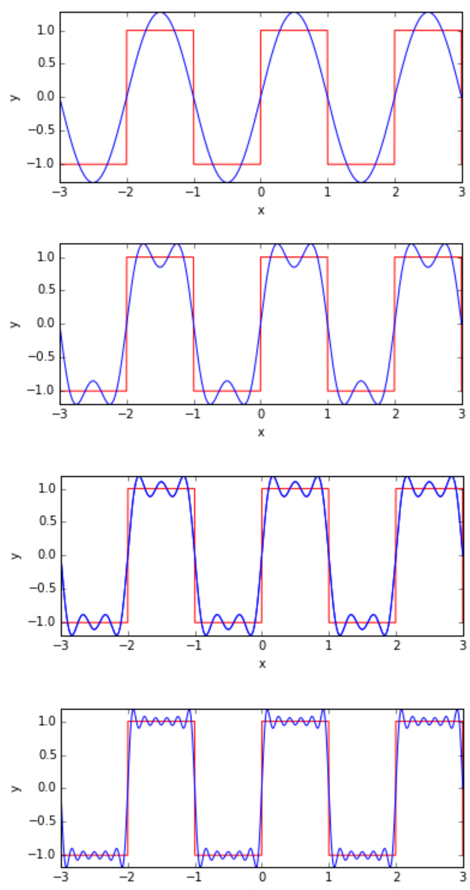

Figure 2.1: The Fourier Series for a step function including one term, three terms, five terms, and nineteen terms. The Fourier Theorem states that the series will converge, reproducing the original function, as the number of terms approaches infinity.

Just as in the vector analogy, we can determine the Fourier coefficients of a function $f$ by computing the inner products:

$$A_n = \langle c_n, f \rangle$$
$$B_n = \langle s_n, f \rangle$$

or, in terms of the inner product integrals:

$$A_n = \sqrt{\frac{2}{L}} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \cos\left(\frac{2\pi n}{L} x\right) dx \tag{2.15}$$

$$B_n = \sqrt{\frac{2}{L}} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \sin\left(\frac{2\pi n}{L} x\right) dx \tag{2.16}$$

Just as in the vector analogy, the inner product determines the correct coefficients only because the basis functions are complete and orthonormal. We will illustrate this with a function that has all of the $B_n$ equal to zero. Start with the completeness equation, but change the index from $n$ to $m$ in order to make the next step clearer.

$$f(x) = \sqrt{\frac{2}{L}} \sum_{m=0}^{\infty} A_m \cos\left(\frac{2\pi m}{L} x\right)$$

Now we apply the prescription in Equation A.13 to both sides of this equation:

$$\begin{aligned}
\sqrt{\frac{2}{L}} \int_{-\frac{L}{2}}^{\frac{L}{2}} f(x) \cos\left(\frac{2\pi n}{L} x\right) dx &= \sqrt{\frac{2}{L}} \int_{-\frac{L}{2}}^{\frac{L}{2}} \left\{ \sqrt{\frac{2}{L}} \sum_{m=0}^{\infty} A_m \cos\left(\frac{2\pi m}{L} x\right) \right\} \cos\left(\frac{2\pi n}{L} x\right) dx \\
&= \sum_{m=0}^{\infty} A_m \left\{ \frac{2}{L} \int_{-\frac{L}{2}}^{\frac{L}{2}} \cos\left(\frac{2\pi m}{L} x\right) \cos\left(\frac{2\pi n}{L} x\right) dx \right\} \\
&= \sum_{m=0}^{\infty} A_m \, \delta_{nm} \\
&= A_n
\end{aligned}$$

Note that the last step follows from the fact that, because of the $\delta_{nm}$ in the product, the only non-zero value in the sum across $m$ is the term for $m = n$.