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

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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:

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

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 is:

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

but keeping in mind that $\psi(x) = 0$ outside of the square well ($[0, a]$) this condition becomes:

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

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:

$$\psi_n(x) = \begin{cases}\sqrt{\frac{2}{a}}\sin(k_n x) & 0\leq x \leq a\\ 0 & \text{otherwise}\end{cases} \tag{2.6}$$

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 ψ_{-n} differs from ψ_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 ψ_n is given by:

$$k_n = \frac{n\pi}{a} = \frac{\sqrt{2mE_n}}{\hbar} \tag{2.7}$$

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2\pi^2\hbar^2}{2ma^2} \tag{2.8}$$

2.3 The Fourier Series

In this section, we'll see how the Fourier Series can be interpreted in the context of a vector space with an inner product. Then we will see how it applies to the infinite square-well problem.

2.3.1 Vector Spaces with Inner Product Spaces

A vector space V is a set whose elements are called vectors, for which an associative and commutative operation of addition is defined, along with a scalar field S with which an associative and distributive operation of scalar multiplication is defined. The only scalar fields we will consider are real numbers ($\mathbb{R}$) and complex numbers ($\mathbb{C}$). The complete set of properties which define a vector field are shown in Table 2.1.

An *inner product* is an operation which returns a scalar for any two vectors x and y. We write the inner product as $\langle x|y\rangle$. If a vector space V has an inner product defined which satisfies conditions I1-I5 in the table, it is an inner product space H as well.

It is left as an exercise to show that the deducible properties D1-D4 listed in the table follow from the other properties.

Table 2.1: Here we define the properties of a vector space V associated with scalar space S, and an inner product space H, using a compact mathematical notation. In case S is the real numbers, just ignore all complex conjugation, e.g. take $\alpha^* = \alpha$.

Useful Math Symbols:

$\forall\, x \in V$	for all x in V (for any vector x)
$\forall\, \alpha \in S$	for all α in S (for any scalar α)
$\exists!\, y$	there exists unique y
s.t.	such that

Properties of Addition:

A1	**Closure**	$\forall x, y \in V$	$(x + y) \in V$
A2	**Commutative**	$\forall x, y \in V$	$x + y = y + z$
A3	**Associative**	$\forall x, y, z \in V$	$(x + y) + z = x + (y + z)$
A4	**Zero**	$\exists!\ 0$ s.t. $\forall x \in V$	$x + 0 = x$
A5	**Inverse**	$\forall x \in V \exists!\ (-x) \in V$ s.t.	$x + (-x) = 0$

Properties of Scalar Multiplication:

M1	**Closure**	$\forall x \in V$ and $\forall \alpha \in S$	$\alpha x \in V$
M2	**Identity**	$\forall x \in V$	$1x = x$
M3	**Associative**	$\forall x \in V$ and $\forall \alpha, \beta \in S$	$\alpha(\beta x) = (\alpha\beta)x$
M4	**Distributive**	$\forall x, y \in V$ and $\forall \alpha \in S$	$\alpha(x + y) = \alpha x + \alpha y$
M5	**Distributive**	$\forall x \in V$ and $\forall \alpha, \beta \in S$	$(\alpha + \beta)x = \alpha x + \beta x$

Deducible Properties:

D1	$\forall x \in V$	$0x = 0$
D2	$\forall x \in V$	$(-1)x = (-x)$

Properties of Inner Products:

I1	$\forall x, y \in H$	$\langle x\vert y\rangle^* = \langle y\vert x\rangle$
I2	$\forall x, y, z \in H$ and $\forall \alpha \in S$	$\langle x\vert \alpha y\rangle = \alpha \langle x\vert y\rangle$
I3	$\forall x, y, z \in H$	$\langle x + y\vert z\rangle = \langle x\vert z\rangle + \langle y\vert z\rangle$
I4	$\forall x \in H$	$\langle x\vert x\rangle \geq 0$
I5	$\forall x \in H$	$\langle x\vert x\rangle = 0$ if and only if $x = 0$

Deducible Properties:

D3	$\forall x, y \in H$ and $\forall \alpha \in S$	$\langle \alpha x\vert y\rangle = \alpha^* \langle x\vert y\rangle$
D4	$\forall x, y, z \in H$	$\langle x\vert y + z\rangle = \langle x\vert y\rangle + \langle x\vert z\rangle$

2.3.2 Euclidean Vector Space

Before turning to the Fourier Series, let's explore how the properties of an abstract vector space apply to the familiar Euclidean vectors. Such a vector is completely specified by its displacement in each spatial direction. Let's see how the properties of Table 2.1. Note that the scalar field S is the real numbers, so we'll just ignore complex conjugation in this example.
We have **vector addition** which satisfies properties A1-A5 of Table 2.1:

- **A1**: $\vec{u} + \vec{v} = \vec{w}$
- **A2**: $\vec{v} + \vec{w} = \vec{w} + \vec{v}$
- **A3**: $\vec{u} + (\vec{v} + \vec{w}) = (\vec{u} + \vec{v}) + \vec{w}$
- **A4**: There is the vector 0 with: $\vec{v} + 0 = \vec{v}$
- **A5**: For every $\vec{v}$ there is $(-\vec{v})$ s.t $\vec{v} + (-\vec{v})$

We also have **scalar multiplication** which satisfies properties M1-M5 and D1,D2:

- **M1:** $a\vec{v} = \vec{v}$
- **M2:** $1\vec{v} = \vec{v}$
- **M3:** $a(b\vec{v}) = (ab)\vec{v}$
- **M4:** $a(\vec{v} + \vec{w}) = a\vec{v} + a\vec{w}$
- **M5:** $(a + b)\vec{v} = a\vec{v} + b\vec{v}$
- **D1:** $(-1)\vec{v} = (-\vec{v})$
- **D2:** $0\vec{v} = 0$

In this vector space, the dot product:

$$\vec{v} \cdot \vec{w} = v_x w_x + v_y w_y + v_z w_z$$

is the inner product which satisfies properties I1-I5:

- **I1:** $\vec{v} \cdot \vec{w} = \vec{w} \cdot \vec{v}$
- **I2:** $\vec{v} \cdot (a\vec{w}) = a\vec{v} \cdot \vec{w}$
- **I3:** $(\vec{u} + \vec{v}) \cdot \vec{w} = \vec{u} \cdot \vec{w} + \vec{v} \cdot \vec{w}$
- **I4:** $\vec{v} \cdot \vec{v} \geq 0$
- **I5:** $\vec{v} \cdot \vec{v} = 0$ if and only if $\vec{v} = 0$
- **D3:** $(a\vec{v}) \cdot \vec{w} = a\,(\vec{v} \cdot \vec{w})$
- **D4:** $\vec{w} \cdot (\vec{u} + \vec{v}) = \vec{w} \cdot \vec{u} + \vec{w} \cdot \vec{v}$

We have a set of *basis vectors*: $\hat{x}$, $\hat{y}$, 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:

$$\begin{aligned} v_x &= \vec{v} \cdot \hat{x} \\ v_y &= \vec{v} \cdot \hat{y} \\ v_z &= \vec{v} \cdot \hat{z} \end{aligned}$$

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.

2.3.3 The Fourier Series

Using the language of inner product 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:

$$\langle f | g \rangle \equiv \int_{-\frac{a}{2}}^{\frac{a}{2}} f(x)\, g(x)\, dx \tag{2.9}$$

The basis vectors are the sine and cosine functions

$$s_n(x) \equiv \sqrt{\frac{2}{a}} \sin\left(\frac{2\pi n}{a} x\right) \tag{2.10}$$

$$c_n(x) \equiv \sqrt{\frac{2}{a}} \cos\left(\frac{2\pi n}{a} x\right) \tag{2.11}$$

which are defined for

$$n = 1, 2, 3, ...$$

plus the constant function:

$$c_0(x) \equiv \sqrt{\frac{1}{a}} \tag{2.12}$$

Note that if it existed, $s_0(x) = 0$ would not be normalizable.

We leave it as an exercise to show that:

$$\begin{aligned}
\langle s_n | s_m \rangle &= \delta_{nm} \\
\langle c_n | c_m \rangle &= \delta_{nm} \\
\langle s_n | c_m \rangle &= 0
\end{aligned} \tag{2.13}$$

for all n and m, but take care that c_0 exists while s_0 does not. For compact notation we use the Kronecker delta symbol:

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

We can write these out explicitly for $n > 0$ and $m > 0$ as:

$$\begin{aligned}
\langle s_n | s_m \rangle &= \frac{2}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} \sin\left(\frac{2\pi n}{a} x\right) \sin\left(\frac{2\pi m}{a} x\right) dx = \delta_{nm} \\
\langle c_n | c_m \rangle &= \frac{2}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} \cos\left(\frac{2\pi n}{a} x\right) \cos\left(\frac{2\pi m}{a} x\right) dx = \delta_{nm} \\
\langle s_n | c_m \rangle &= \frac{2}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} \sin\left(\frac{2\pi n}{a} x\right) \cos\left(\frac{2\pi m}{a} x\right) dx = 0
\end{aligned} \tag{2.14}$$

leaving the special case for c_0 (and still keeping $n > 0$):

$$\begin{aligned}
\langle c_n | c_0 \rangle &= \frac{\sqrt{2}}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} \cos\left(\frac{2\pi n}{a} x\right) dx = 0 \\
\langle s_n | c_0 \rangle &= \frac{\sqrt{2}}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} \sin\left(\frac{2\pi n}{a} x\right) dx = 0 \\
\langle c_0 | c_0 \rangle &= \frac{1}{a} \int_{-\frac{a}{2}}^{\frac{a}{2}} dx = 0
\end{aligned} \tag{2.15}$$

Fourier's Theorem states that these orthonormal basis functions are complete for the vector space of periodic functions with period a. That is, if $f(x)$ has the property that:

$$f(x) = f(x + a)$$

then $f(x)$ can be written as a sum of the orthonormal basis vectors:

$$f(x) \;=\; \sum_{n=0}^{\infty} A_n\, c_n(x) \;+\; \sum_{n=1}^{\infty} B_n\, s_n(x) \tag{2.16}$$

or explicitly in terms of sine and cosine functions:

$$f(x) = A_0\sqrt{\frac{1}{a}} + \sqrt{\frac{2}{a}}\sum_{n=1}^{\infty}\left[A_n \cos\left(\frac{2\pi n}{a}\, x\right) + B_n \sin\left(\frac{2\pi n}{a}\, x\right)\right] \tag{2.17}$$

The values A_n and B_n are called *Fourier coefficients*. Technically the Nth 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 $f(x)$. The demonstration of completeness is optional reading, available in the Appendix.

We can write things a bit more neatly:

$$f(x) = a_0 + \sum_{n=1}^{\infty}\left[a_n \cos\left(\frac{2\pi n}{a}\, x\right) + b_n \sin\left(\frac{2\pi n}{a}\, x\right)\right] \tag{2.18}$$

where:

$$\begin{aligned} a_0 &= \sqrt{\frac{1}{a}} A_0 \\ a_n &= \sqrt{\frac{2}{a}} A_n \\ b_n &= \sqrt{\frac{2}{a}} B_n \end{aligned}$$

but at the cost of obscuring the role of the orthonormal basis functions.

For a visual example of the Fourier Series, the first terms of the Fourier Series for a step function are shown in Fig. 2.1.

2.3.4 Determining Fourier Coefficients

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

$$\begin{aligned} A_n &= \langle c_n | f \rangle \\ B_n &= \langle s_n | f \rangle \end{aligned}$$

or, in terms of the inner product integrals and sine and cosine functions:

$$\begin{aligned} A_0 &= \sqrt{\frac{1}{a}} \int_{-\frac{a}{2}}^{\frac{a}{2}} f(x)\, dx \\ A_n &= \sqrt{\frac{2}{a}} \int_{-\frac{a}{2}}^{\frac{a}{2}} \cos\left(\frac{2\pi n}{a}\, x\right)\, f(x)\, dx \\ B_n &= \sqrt{\frac{2}{a}} \int_{-\frac{a}{2}}^{\frac{a}{2}} \sin\left(\frac{2\pi n}{a}\, x\right)\, f(x)\, dx \end{aligned}$$

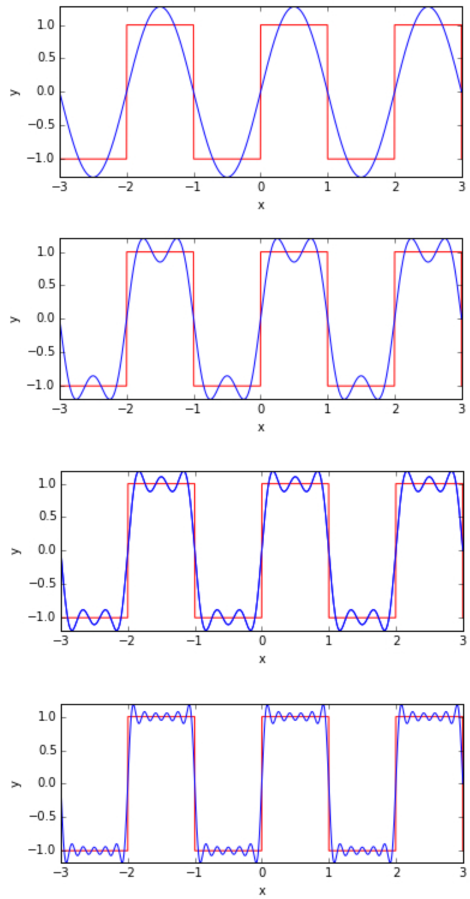

Figure 2.1: The Fourier Series for a step function including one term, three terms, five terms, and nineteen terms. The Fourier Theorem states that the series will converge, reproducing the original function, as the number of terms approaches infinity.

The inner product determines the correct coefficients only because the basis functions are complete and orthonormal. To see how this works, start with the completeness equation but replace n with m for clarity later:

$$f(x) \;=\; \sum_{m=0}^{\infty} A_m\, c_m(x) \;+\; \sum_{m=1}^{\infty} B_m\, s_m(x)$$

Then calculate:

$$\begin{aligned}
\langle c_n|f\rangle &= \sum_{m=0}^{\infty} A_m \;\langle c_n|c_m\rangle \;+\; \sum_{m=1}^{\infty} B_m \;\langle c_m|s_m\rangle \\
&= \sum_{m=0}^{\infty} A_m \;\delta_{nm} \;+\; \sum_{m=1}^{\infty} B_m \;0 \\
\langle c_n|f\rangle &= A_n
\end{aligned}$$

Note that the last step follows from the fact that, because of the δ_{nm} in the product, the only non-zero value in the sum across m is the term for $m = n$. It is left as an exercise to work this out for $\langle s_n|f\rangle$.

2.3.5 Application of Fourier Series to Infinite Well

For the potential well, we have a wave function $\psi(x)$ which meets the boundary conditions $\psi(0) = \psi(a) = 0$. We define a helper function:

$$f(x) = \begin{cases} \psi(x) & 0 \leq x \leq a \\ -\psi(-x) & -a \leq x < 0 \end{cases}$$

It is an odd function by construction: $f(-x) = -f(x)$. Since f(a) = f(-a) = 0, we can consider it to be a periodic function with period $2a$. To evaluate it's Fourier series, we'll only need to evaluate it in the region $[-a, a]$ where it is defined[1].

For $f(x)$ the Fourier coefficients of the cosines all vanish:

$$\begin{aligned} A_0 &= \sqrt{\frac{1}{2a}} \int_{-a}^{a} f(x)\, dx = 0 \\ A_n &= \sqrt{\frac{1}{a}} \int_{-a}^{a} \cos\left(\frac{\pi n}{a} x\right) f(x)\, dx = 0 \end{aligned}$$

where we have put $a \to 2a$ in the original formulas, since the period of our function is now $2a$. So the Fourier Series for $f(x)$ contains only sines:

$$\begin{aligned} f(x) &= \sqrt{\frac{1}{a}} \sum_{n=1}^{\infty} B_n \sin\left(\frac{\pi n}{a} x\right) \\ &= \sum_{n=1}^{\infty} \left(\frac{B_n}{\sqrt{2}}\right) \left(\sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{a} x\right)\right) \end{aligned}$$

We determine the Fourier coefficients for the sines from:

$$B_n = \sqrt{\frac{1}{a}} \int_{-a}^{a} \sin\left(\frac{\pi n}{a} x\right) f(x)\, dx = 0$$

but since the integrand is now even, the integral does not vanish, and in fact, we need only integrate in $[0, a]$ and multiply by a factor of two:

$$B_n = 2 \times \sqrt{\frac{1}{a}} \int_{0}^{a} \sin\left(\frac{\pi n}{a} x\right) f(x)\, dx = 0$$

$$c_n \equiv \frac{B_n}{\sqrt{2}} = \int_0^a \left(\sqrt{\frac{2}{a}} \sin\left(\frac{\pi n}{a} x\right)\right) f(x) dx$$

And since we are now integrating only from $[0, a]$ then

$$f(x) = \psi(x)$$

[1] If you prefer, you can imagine making it truly periodic by just stamping out a copy of $f(x)$ from $[-a, a]$ into $[a, 3a]$, and so on.

and we can rewrite these equations in terms of

$$\psi_n(x) = \begin{cases} \sqrt{\dfrac{2}{a}}\,\sin(k_n x) & 0 \le x \le a \\ 0 & \text{otherwise} \end{cases} \tag{2.19}$$

where

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

Any wave function can be expressed as a linear combination of these basis functions:

$$\psi(x) = \sum_{n=1}^{\infty} c_n \psi_n(x) \tag{2.20}$$

when $0 \le x \le a$ and $\psi(x) = 0$ otherwise. And

$$c_n = \langle \psi_n | \psi \rangle = \int_0^a \psi_n(x)\,\psi(x)\,dx$$

2.4 Insights from the Infinite Square Well

Let's recap what we have learned so far. By assuming that we could find solutions of the form

$$\Psi(x,t) = \psi(x)\,\phi(t)$$

we have indeed found an infinite number of solutions to the TISE for the Infinite Square Well potential:

$$\hat{H}\,\psi_n(x) = E_n\,\psi_n(x)$$

for $n = 1, 2, 3, \ldots$. Each of these solutions has an associated time dependent "wiggle factor":

$$\phi_n(t) = \exp(-\frac{iE_n t}{\hbar})$$

so that the total wave equation is:

$$\Psi_n(x,t) = \exp(-\frac{iE_n t}{\hbar})\,\psi_n(x)$$

We saw that these are **stationary states** (the expectation values are constant in time) and they are **states of definite energy** (every measurement of their energy will yield the results E_n).

By design, the $\Psi_n(x,t)$ are solutions to the (time dependent) SE. It's instructive to see exactly how that works:

$$\begin{aligned}
\hat{H}\,\Psi_n(x,t) &= -i\hbar\frac{\partial\Psi}{\partial t} \\
\exp(-\frac{iE_n t}{\hbar})\;\hat{H}\;\psi_n(x) &= -i\hbar\psi_n(x)\,\frac{d}{dt}\exp(-\frac{iE_n t}{\hbar}) \\
\exp(-\frac{iE_n t}{\hbar})\;E_n\;\psi_n(x) &= -i\hbar\psi_n(x)\,\frac{-iE_n}{\hbar}\exp(-\frac{iE_n t}{\hbar}) \\
E_n\Psi(x,t) &= E_n\Psi(x,t)
\end{aligned}$$

Our detour into the Fourier series has given us a crucial additional insight. The $\psi_n(x)$ are also a complete orthonormal basis for the Fourier series of any function that meets the boundary conditions for this problem. That means that we have in fact already found the *general solution* to this problem.

Suppose the initial state of a particle is $\Psi(x,0) \equiv \psi_i(x)$. This can be absolutely any function so long as it vanishes outside of $[0,a]$ and it is properly normalized. Our job is to find $\Psi(x,t)$ that satisfies the SE for all future times. We calculate the Fourier coefficients of $\psi_i(x)$ as:

$$c_n = \langle \psi_n | \psi_i \rangle = \int_0^a \psi_n(x)\, \psi_i(x)\, dx$$

and by Fourier's theorem, we know that:

$$\Psi(x,0) = \sum_{n=0}^{\infty} c_n \psi_n(x)$$

But what about $\Psi(x,t)$? It really couldn't be any simpler:

$$\begin{aligned} \Psi(x,t) &= \sum_{n=0}^{\infty} c_n \Psi_n(x,t) \\ &= \sum_{n=0}^{\infty} c_n \exp(-\frac{iE_n t}{\hbar})\, \psi_n(x) \end{aligned}$$

It is left as an exercise to show explicitly that $\Psi(x,t)$ as defined here does satisfy the time-dependent SE and is equal to $\psi_i(x)$ at $t=0$.

Almost unbelievably, there is still some insight to be gleamed from this simple example. We specified that $\Psi(x,0)$ is normalized, and we showed that the SE preserves normalization, so we know that $\Psi(x,t)$ is normalized as well:

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

And plugging in our Fourier Series solution for $\Psi(x,t)$:

$$\begin{aligned} 1 &= \int_{-\infty}^{+\infty} \Psi^*(x,t)\Psi(x,t)\, dx \\ &= \int_{-\infty}^{+\infty} \left(\sum_{n=1}^{\infty} c_n^* \Psi_n^*(x,t) \right) \left(\sum_{m=1}^{\infty} c_m \Psi_m(x,t) \right)\, dx \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m \exp\left(\frac{i(E_n - E_m)t}{\hbar} \right) \int_{-\infty}^{+\infty} \psi_n^*(x)\psi_m(x)\, dx \\ &= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m \exp\left(\frac{i(E_n - E_m)t}{\hbar} \right) \delta_{nm} \end{aligned}$$

so that

$$\sum_{n=1}^{\infty} |c_n|^2 = 1 \tag{2.21}$$

We can also calculate:

$$\begin{aligned}
\langle H \rangle &= \int_{-\infty}^{+\infty} \Psi^*(x,t) \hat{H} \Psi(x,t)\, dx \\
&= \int_{-\infty}^{+\infty} \left(\sum_{n=1}^{\infty} c_n^* \Psi_n^*(x,t) \right) \hat{H} \left(\sum_{m=1}^{\infty} c_m \Psi_m(x,t) \right) dx \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m \exp\left(\frac{i(E_n - E_m)t}{\hbar} \right) \int_{-\infty}^{+\infty} \psi_n^*(x) \hat{H} \psi_m(x)\, dx \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m \exp\left(\frac{i(E_n - E_m)t}{\hbar} \right) \int_{-\infty}^{+\infty} \psi_n^*(x) E_m \psi_m(x)\, dx \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m \exp\left(\frac{i(E_n - E_m)t}{\hbar} \right) E_m \int_{-\infty}^{+\infty} \psi_n^*(x) \psi_m(x)\, dx \\
&= \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} c_n^* c_m \exp\left(\frac{i(E_n - E_m)t}{\hbar} \right) E_m \delta_{nm}
\end{aligned}$$

so that

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n \tag{2.22}$$

Recall from our review of statistics that:

$$\langle H \rangle = \sum_{n=1}^{\infty} P(n) E_n \tag{2.23}$$

where $P(n)$ is the probability of observing the particle in state n.

This allows us to identify $|c_n|^2$ as the probability of observing the particle with energy E_n.

Appendix A

Proofs of Completeness of Trigonometric Functions

A.0.1 The Dirac Delta Function

These proofs make extensive use of the Dirac delta function, $\delta(x)$, which is zero everywhere but at $x = 0$, where it is infinite. Mathematically, the delta function only makes formal sense inside an integral, where it has the following defining properties:

$$\int_{-\infty}^{\infty} f(x')\,\delta(x - x')\,dx' = f(x) \tag{A.1}$$

$$\int_{-\infty}^{\infty} \delta(x)\,dx = 1 \tag{A.2}$$

The delta function simply picks out from the integral the one value of the integrand which makes the argument of the delta function zero. This makes intuitive sense, because the delta function is zero everywhere else. The second equation shows the normalization of the delta function, which follows from the first if you take $f(x) = 1$.

A.0.2 The completeness of the sines and cosines

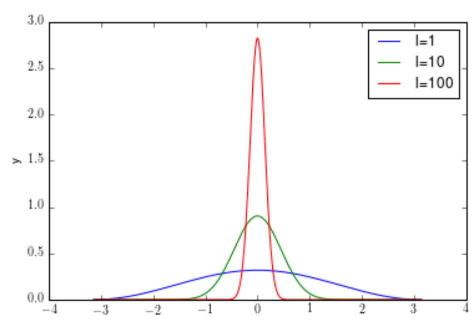

Figure A.1: The function $h_\ell(x)$ for increasingly large values of ℓ.

To demonstrate the completeness of sines and cosines[1] we construct a peculiar but useful set of

[1]This proof taken from http://web.mit.edu/jorloff/www/18.03-esg/notes/fourier-complete.pdf

functions defined for $\ell = 1, 2, 3, ...$:

$$h_\ell(x) = c_\ell \left(\frac{1+\cos(x)}{2}\right)^\ell$$

We chose each factor c_ℓ such that:

$$\int_{-\pi}^{\pi} h_\ell(x) = 1$$

The shape of h_ℓ is shown in Fig. A.1. As ℓ increases, h_ℓ becomes more and more narrow at $x = 0$, while the normalization is as in Equation A.2. It looks more and more like the delta function:

$$\lim_{\ell\to\infty} h_\ell(x) = \delta(x)$$

It has one other important feature: $h_\ell(x)$ is simply a sum of cosines of nx with coefficients that don't depend on x. To see how this can be, note that we can always turn a product of cosines into a sum via the trigonometric identity:

$$\cos\alpha\cos\beta = \frac{1}{2}\{\cos(\alpha-\beta) + \cos(\alpha+\beta)\}.$$

So, for instance, we can write:

$$\begin{aligned} h_2(x) &= \frac{c_2}{4} + \frac{c_2\cos(x)}{2} + \frac{c_2\cos^2(x)}{4} \\ &= \frac{c_2}{4} + \frac{c_2\cos(x)}{2} + \frac{c_2\cos(2x)}{8} \end{aligned}$$

This property implies that the function $h_\ell(x-a)$ for some constant a is simply a sum of *both* sines and cosines of nx with coefficients that don't depend on x, as:

$$\cos(nx - na) = \cos(nx)\cos(na) + \sin(nx)\sin(na).$$

With this technology in hand we are ready to demonstrate the completeness of the sines and cosines. For simplicity, it suffices to consider only functions with period $L = 2\pi$ (i.e. $k_n = n$). The general case can then be inferred by transformation of coordinates. Consider a real function $f(x)$ which is periodic for $L = 2\pi$. For now just define the function $F(x)$ to be the infinite series:

$$F(x) \equiv a_0 + \sum_{n=1}^{\infty}\{a_n\cos(nx) + b_n\sin(nx)\}. \tag{A.3}$$

This is the compact form of the Fourier Series for this special case $L = 2\pi$, so $k_n = n$. We assume the coefficients are determined in the usual way:

$$\begin{aligned} a_n &= \frac{2}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} f(x)\cos(nx)\,dx \\ b_n &= \frac{2}{L}\int_{-\frac{L}{2}}^{\frac{L}{2}} f(x)\sin(nx)\,dx. \end{aligned}$$

We need to show that $F(x) = f(x)$, or

$$g(x) = F(x) - f(x) = 0$$

The proof hinges on the fact that $F(x)$ and $f(x)$ have the same Fourier coefficients, so that:

$$\begin{aligned}
\int_{-\pi}^{\pi} g(x)\sin(nx)dx &= \int_{-\pi}^{\pi} F(x)\sin(nx)dx - \int_{-\pi}^{\pi} f(x)\sin(nx)dx \\
&= b_n - b_n \\
&= 0 \\
\int_{-\pi}^{\pi} g(x)\cos(nx)dx &= \int_{-\pi}^{\pi} F(x)\cos(nx)dx - \int_{-\pi}^{\pi} f(x)\cos(nx)dx \\
&= a_n - a_n \\
&= 0
\end{aligned}$$

This shows that the integral of $g(x)$ times any sine or cosine is zero. But our special function $h_\ell(x-a)$ function is just a sum of sines and cosines of nx for any value of a. This means that:

$$\int_{-\pi}^{\pi} h_\ell(x-a)g(x)dx = 0$$

If we take the limit as $\ell \to \infty$, we obtain:

$$\begin{aligned}
\int_{-\pi}^{\pi} \delta(x-a)g(x)dx &= 0 \\
g(a) &= 0
\end{aligned}$$

Since this is true for any value of a, we have $g(x) = 0$ and so $F(x) = f(x)$.

A.0.3 The orthogonality and completeness of the complex exponential function

The first thing we need to show is that:

$$\frac{1}{2\pi}\int_{-\infty}^{\infty} \exp(ikx)\,dk = \delta(x) \tag{A.4}$$

To see this we first calculate:

$$\begin{aligned}
\frac{1}{2\pi}\int_{-a}^{a} \exp(ikx)\,dk &= \frac{1}{2\pi}\frac{\exp(iax) - \exp(-iax)}{ix} \\
&= \frac{1}{\pi}\frac{\sin(ax)}{x} \\
&= \frac{a}{\pi}\operatorname{sinc}(ax)
\end{aligned}$$

An integration shows that:

$$\int_{-\infty}^{\infty} \frac{a}{\pi}\operatorname{sinc}(ax)\,dx = 1 \tag{A.5}$$

exactly as needed for Equation A.2.

Fig. A.2 shows that this function peaks at zero and becomes more and more narrow for progressively larger values of a. Since it has the correct normalization, we conclude that:

$$\begin{aligned}\frac{1}{2\pi}\int_{-\infty}^{\infty}\exp(ikx)\,dk &= \lim_{a\to\infty}\frac{1}{2\pi}\int_{-a}^{a}\exp(ikx)\,dk \\ &= \lim_{a\to\infty}\frac{a}{\pi}\,\mathrm{sinc}(ax) \\ &= \delta(x)\end{aligned}$$

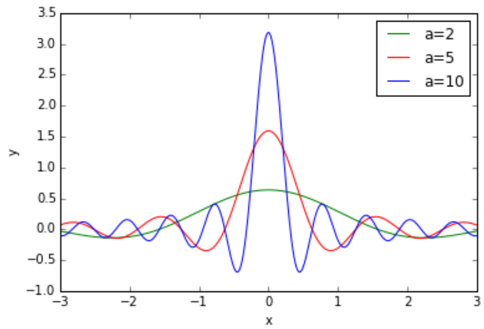

Figure A.2: The function $a\,\mathrm{sinc}(ax)/\pi$ for progressively larger values of a. As $a \to \infty$, this function approaches the delta function $\delta(x)$.

We are now fully equip to show that the complex exponential functions:

$$e_k = \frac{1}{\sqrt{2\pi}}\exp(ikx)$$

are orthonormal. Calculating the inner product

$$\begin{aligned}\langle e_k, e_{k'}\rangle &= \int_{-\infty}^{\infty}\frac{1}{\sqrt{2\pi}}\exp(-ikx)\frac{1}{\sqrt{2\pi}}\exp(ik'x)\,dx \\ &= \frac{1}{2\pi}\int_{-\infty}^{\infty}\exp\{i(k'-k)x\}\,dx \\ &= \delta(k-k')\end{aligned}$$

where we have used Equation A.5 but with the roles of x and k exchanged. To prove completeness, we can now show that:

$$\begin{aligned}\Psi(x) &= \int_{-\infty}^{\infty}\Psi(x')\,\delta(x-x')\,dx' \\ &= \int_{-\infty}^{\infty}f(x')\left\{\frac{1}{2\pi}\int_{-\infty}^{+\infty}\exp\{ik(x-x')\}\,dk\right\}\,dx' \\ &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\left\{\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{+\infty}f(x')\exp(-ikx')\,dx'\right\}\exp(ikx)\,dk \\ &= \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\widetilde{\Psi}(k)\exp(ikx)\,dk\end{aligned}$$

where:

$$\widetilde{\Psi}(k) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty}\Psi(x)\,\exp(-ikx)\,dx$$