PHYS4210: Quantum Mechanics

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1 Intro

- From the double slit experiment, we can discover some crazy stuff from Quantum Mechanics:
  - Using a normal (classical) gun, we don't find any interference in the resulting patterns, which is exactly what we would expect.
  - Using a a wave gun, we do find interference, but this is also what we expect, since at the time, there was plenty of study on waves.
  - If we use an electron gun, we also in fact find interference, but this is not what we expect. The electron-as-a-particle idea clearly cannot stand!
- Normal wave intensity is given as the square of the height, which is a type of amplitude. In a similar vein, we can define probability distributions for our electrons as a more abstract amplitude:

$$P = |\psi|^2. \tag{1.1}$$

- This is all we can know: the probaility of something happening (Schrodinger's Cat thought experiment). Only once we make a full measurement can we find out for sure that state of something.
- So, the electron, before measurement, is a wave, but after measurement, it is a particle.

2 The Schrödinger Equation

- To find the aforementioned ψ, we need the **Time-Dependent Schrodiner Equation (TDSE)**:

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

  or

$$i\hbar\frac{\partial\Psi}{\partial t} = \left(-\frac{\hbar}{2m}\frac{\partial^2}{\partial x^2} + V\right)\Psi, \tag{2.2}$$

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi, \tag{2.3}$$

  where $\hat{H}$ is the **Hamiltonian operator**. This is analogous to the classical "master" equation: Newton's Second Law:

$$-\frac{\mathrm{d}V}{\mathrm{d}r} = m\frac{\mathrm{d}^2x}{\mathrm{d}t^2}. \tag{2.4}$$

- However, this is often *extremely* hard to solve even for seemingly simple systems. One simplification we make is when the potential is not dependent on time, we can then make the **Time-Independent Schrodinger Equation (TISE)**:

$$E\psi = \bar{H}\psi, \tag{2.5}$$

  where E is the energy of that particular state, called a **stationary state**. This ψ is lowercase to signify that this is technically a different equation it is satisfying. Ψ is the total wavefunction with the time-dependent part included.
  - From here on out, we will continue to use the lowercase ψ just for ease. The distinction should be clear if and when it is necessary.
- Born's interpretation of this wavefunction is that

$$|\psi(x,t)|\mathrm{d}x \tag{2.6}$$

  is the probaility of finding a particle between x and $x + \mathrm{d}x$.

- Thus, to determine the probability of finding a particle between $x = a, b$,

$$P(x \in [a,b]) = \int \mathrm{d}x \, |\phi(x,t)|^2. \tag{2.7}$$

- Perhaps one of the more sensible and surprisingly important concept here is that our particle must be somewhere. This means that the total probaility over all space must be equal to one:

$$\int_{-\infty}^{\infty} \mathrm{d}x \, |\psi(x,t)| = 1. \tag{2.8}$$

- This will turn out to be a very important condition to normalize an arbitrary wavefunction. For instance, for some wavefunction ψ, if the above relation is not satisfied, we know that we can simply multiply by a constant and have it still satisfy the SE, so we have $A\psi$. We can then use the normalization condition to determine what A must be.

- If the above integral of some wavefunction turns out to be something non-normalizable, like infinity or zero, then it cannot be physical, and we will just ignore it.

- A nice property of this condition is that we can normalize it at one time, say $t = 0$, so that $\psi(x, 0)$ is normalized. Then, we don't have to normalize it again; it will say normalized for all time.

- We can prove this now. Let's start with two copies of the SE. For the first, we will multiply it (from the left) by ψ^*:

$$i\hbar\psi^* \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m}\psi^* \frac{\partial^2 \psi}{\partial x^2} + V\psi^*\psi. \tag{2.9}$$

- For the second copy, we will complex conjugate it the multiply it by ψ:

$$i\hbar\psi \frac{\partial \psi^*}{\partial t} = \frac{\hbar^2}{2m}\psi \frac{\partial^2 \psi *}{\partial x^2} - V\psi\psi^*. \tag{2.10}$$

- Now we add the two together:

$$i\hbar\left(\psi^* \frac{\partial \psi}{\partial t} + \psi \frac{\partial \psi^*}{\partial t}\right) = -\frac{\hbar^2}{2m}\left(\psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2}\right) + V(\psi^*\psi - \psi\psi^*). \tag{2.11}$$

- The potential term will be zero obviously. Now, we can "undo" the product rule on the left to obtain:

$$i\hbar \frac{\partial}{\partial t}(\psi^*\psi) = i\hbar \frac{\partial |\psi|^2}{\partial t} = -\frac{\hbar^2}{2m}\left(\psi^* \frac{\partial^2 \psi}{\partial x^2} - \psi \frac{\partial^2 \psi^*}{\partial x^2}\right). \tag{2.12}$$

- Now, we can undo one of the product rules on the right-hand side to obtain:

$$i\hbar \frac{\partial |\psi|^2}{\partial t} = -\frac{\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right]. \tag{2.13}$$

- Let's integrate both sides over all space:

$$\int_{-\infty}^{\infty} \mathrm{d}x \; i\hbar \frac{\partial |\psi|^2}{\partial t} = \int_{-\infty}^{\infty} \mathrm{d}x \; -\frac{\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^* \frac{\partial \psi}{\partial x} - \psi \frac{\partial \psi^*}{\partial x}\right]. \tag{2.14}$$

- On the left, since the derivative and integral are unrelated units, we can pull the time derivative out and it'll become a total derivative. On the left, the integral and derivative cancel and we simply evaluate the quantity at the limits. However, the limits are $\pm\infty$, and we know that the wavefunction must vanish at these limits, so the entire right hand side vanishes.

- All we are left with then, is:

$$\frac{\mathrm{d}}{\mathrm{d}t}\int_{-\infty}^{\infty}\mathrm{d}x\,|\psi|^2 = 0. \tag{2.15}$$

- The integral part is our normalization condition, and for its time derivative to be zero suggests that this normalization does not change with time, for any wavefunction.

Example 2.1:

At time $t = 0$, a particle is represented by a wave function:

$$\psi(x,0) = \begin{cases} A\left(\frac{x}{a}\right) & \text{for } 0 \le x \le a \\ A\left(\frac{b-x}{b-a}\right) & \text{for } a \le x \le b \\ 0 & \text{otherwise} \end{cases} \tag{2.16}$$

a) Normalize ψ. That is, find A in terms of a and b.

- All we need to do here is just plug in to our normalization condition and find a relation for A:

$$\int_{-\infty}^{\infty}\mathrm{d}x\,|\psi|^2 = \int_0^a \mathrm{d}x\,A^2\frac{x^2}{a^2} + \int_a^b \mathrm{d}x\,A^2\left(\frac{b-x}{b-a}\right)^2 = 1. \tag{2.17}$$

$$\frac{A^2}{a^2}\int_0^a \mathrm{d}x\,x^2 + \frac{A^2}{(b-a)^2}\int_a^b \mathrm{d}x\,(b-x)^2 = 1 \tag{2.18}$$

$$\frac{1}{3}A^2a + \frac{1}{3}A^2(b-a) = 1 \tag{2.19}$$

$$A^2b = 3, \tag{2.20}$$

so

$$\boxed{A = \sqrt{\frac{3}{b}}}. \tag{2.21}$$

b) What is the probability of finding the particle to the left of a?

- This is simple: we just integrate the wavefunction squared from 0 to a (technically from $-\infty$ to a, but since the wavefunction is only non-zero starting at $x = 0$, we can just say that)

$$\int_0^a \mathrm{d}x\,|\psi|^2 = \frac{3}{a^2b}\int_0^a \mathrm{d}x\,x^2 = \boxed{\frac{a}{b}}. \tag{2.22}$$

As a sort of confirmation, if we have that $a = b$, then we are integrating over the entire non-zero area of the wavefunction, and the result is 1, as we expect. If $b = 2a$, we have that the probability is $1/2$, which also makes sense, as this is just half.

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3 Short Refresher on Probability

In this section, we briefly recap some important quantities and formulas in probability that are relevant for us in quantum mechanics. Derivations and more discussion can be found in the first chapter of Griffiths.

- First, given a random sample, the probability that we pick an element j from the sample is

$$\rho(j) = \frac{N(j)}{N}, \tag{3.1}$$

  where $N(j)$ is the number of times j appears in the sample, and N is the total number of elements in the sample.

- We expect, intuitively, that the sum of the probabilities of all the elements in the sample would be equal to 1, and that is exactly what we get. Quantitatively:

$$\sum_j \rho(j) = 1. \tag{3.2}$$

- The next interesting quantities we will want to look at are averages. The average of some *observable* j (same letter, but slightly different meaning now), such as the age in a group of people in a room, is given by the following:

$$\langle j \rangle = \sum_j j\rho(j). \tag{3.3}$$

  We can see this with an example, continuing with the example of ages of people in a room. Let's say there are three 21 year olds, four 22 year olds, and five 23 year olds. We do the following:

$$\langle j \rangle = \frac{3 \cdot 21 + 4 \cdot 22 + 5 \cdot 23}{12} = \frac{3}{12} \cdot 21 + \frac{4}{12} \cdot = \frac{5}{12} \cdot 23 = \sum_j j \frac{N(j)}{j}.$$

  By virtue of Eq. (3.1), the above becomes Eq. (3.3).

- In a similar manner, we can determine the average of j^2:

$$\langle j^2 \rangle = \sum_j j^2 \rho(j). \tag{3.4}$$

- Generally, then, the average of any function of j is

$$\langle f(j) \rangle = \sum_j f(j)\rho(j). \tag{3.5}$$

- Jumping to the continuous case (and into physics world), our interpretation of $\rho(x)$ where x is some continuous variable, is that the quantity

$$\rho(x)\mathrm{d}x \tag{3.6}$$

  is the probability of finding a particle between x and $x + \mathrm{d}x$. So,

$$P(x \in [a, b]) = \int_a^b \rho(x)\mathrm{d}x. \tag{3.7}$$

- As in the discrete case, the particle has to be *somewhere*, so we expect that if we integrate the probability over all space the result must be one:

$$\int_{-\infty}^{\infty} \rho(x) = 1 \, \mathrm{d}x. \tag{3.8}$$

- Further, the idea of averages carries over as one would expect:

$$\langle f(x)\rangle = \int_a^b f(x)\rho(x)\,\mathrm{d}x. \tag{3.9}$$

- Jumping back to quantum, we know that Born's interpretation of the quantum wavefunction ψ is that its (modulus) square is the probability, so

$$\langle f(x)\rangle = \int_a^b f(x)|\psi|^2\,\mathrm{d}x. \tag{3.10}$$

- Looking specifically at the average of x (and dropping integration limits until we know where we want to integrate):

$$\langle x\rangle = \int x|\psi|^2\,\mathrm{d}x. \tag{3.11}$$

- Since $p = mv = m\mathrm{d}x/\mathrm{d}t$,

$$\begin{aligned}\langle p\rangle &= m\frac{\mathrm{d}}{\mathrm{d}t}\int x|\psi|^2\,\mathrm{d}x,\\ &= m\int x\frac{\partial}{\partial t}|\psi|^2\,\mathrm{d},\end{aligned}$$

  where, when bringing the total time derivative inside the integral, we now have x dependence, so the total derivative becomes a partial derivative.

- Now, from the SE:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V\psi, \tag{3.12}$$

$$\frac{\partial\psi}{\partial t} = i\frac{\hbar}{2m}\frac{\partial^2\psi}{\partial x^2} - \frac{i}{\hbar}V\psi. \tag{3.13}$$

  The complex conjugate is:

$$\frac{\partial\psi^*}{\partial t} = -i\frac{\hbar}{2m}\frac{\partial^2\psi^*}{\partial x^2} + \frac{i}{\hbar}V\psi. \tag{3.14}$$

  Now, multiplying (3.13) by ψ^* (in front) and (3.14) by ψ (also in front), we get:

$$\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t} = \frac{i\hbar}{2m}\psi^*\frac{\partial^2\psi}{\partial x^2} - \frac{i}{\hbar}V\psi^*\psi - \frac{i\hbar}{2m}\psi\frac{\partial^2\psi^*}{\partial x^2} + \frac{i}{\hbar}V\psi\psi^*.$$

  The potential terms will cancel, since $\psi\psi^* = \psi^*\psi$, so we have:

$$\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t} = \frac{i\hbar}{2m}\left[\psi^*\frac{\partial^2\psi}{\partial x^2} - \psi\frac{\partial^2\psi^*}{\partial x^2}\right].$$

- We can do an inverse product-rule now to bring out one of the x derivatives:

$$\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t} = \frac{i\hbar}{2m}\frac{\partial}{\partial x}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right].$$

- We have now simplified this as much as we really can; the expression on the left side of the equals sign is just the time derivative of the modulus square of the wavefunction, so we can just replace it in the integral with the expression on the right hand side of the equals sign:

$$m\int x\frac{\partial}{\partial t}|\psi|^2\,\mathrm{d}x = \frac{i\hbar}{2}\int x\frac{\partial}{\partial x}\left[\psi^*\frac{\partial\psi}{\partial x} - \psi\frac{\partial\psi^*}{\partial x}\right]\mathrm{d}x.$$

- If we do integration by parts, we get:

$$\to -\frac{i\hbar}{2}\int \frac{\mathrm{d}x}{\mathrm{d}x}\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)\,\mathrm{d}x+\left[x\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)\right]_{-\infty}^{\infty}.$$

  But, since by construction we have that the wavefunction vanishes at infinity, the second term is just zero. Further, obviously, $\mathrm{d}x/\mathrm{d}x = 1$, so:

$$\langle p\rangle = -\frac{i\hbar}{2}\int\left(\psi^*\frac{\partial\psi}{\partial x}-\psi\frac{\partial\psi^*}{\partial x}\right)\,\mathrm{d}x.$$

- We can do integration by parts on the second term this time to get

$$\langle p\rangle = -\frac{i\hbar}{2}\int\left(\psi^*\frac{\partial\psi}{\partial x}+\psi^*\frac{\partial\psi}{\partial x}\right)\,\mathrm{d}x-\psi^*\psi|_{infty}^{\infty},$$

  and, again, the second term will vanish, so all we are left with is

$$\boxed{\langle p\rangle = -i\hbar\int\psi^*\frac{\partial\psi}{\partial x}\,\mathrm{d}x}. \tag{3.15}$$

- However, we can rewrite this in this way:

$$\langle p\rangle = \int\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,\mathrm{d}x,$$

  and similarly, for x,

$$\langle x\rangle = \int\psi^* x\psi\,\mathrm{d}x.$$

- Here, we have sort of sandwiched these quantities in between the wave function and its complex conjugate. The quantity in the sandwich is the **operator**, and it *acts* on a wavefunction. It is much more clear to see this in the case of the momentum operator, since it contains a derivative, the most well-known operator.

- In Dirac notation, which will hopefully be introduced at some point, these are condensed into the following notation:

$$\int\psi^* x\psi\,\mathrm{d}x = \langle\psi^*|\,\hat{x}\,|\psi\rangle\,,\ \text{and}\ \int\psi^*\left(-i\hbar\frac{\partial}{\partial x}\right)\psi\,\mathrm{d}x = \langle\psi^*|\,\hat{p}\,|\psi\rangle\,.$$

- So, we have retrieved the quantum prescription:

$$\hat{p} = -i\hbar\frac{\partial}{\partial x}.$$

- Interestingly, plugging this into the kinetic energy relation $T = p^2/2m$ nets us

$$\hat{T} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}, \tag{3.16}$$

- Which is exactly what shows up in the SE.

3.1 The Heisenberg Uncertainty Principle

- The **Heisenberg Uncertainty Principle** gives the following relation:

$$\boxed{\sigma_x \sigma_p \geq \frac{\hbar}{2}.} \tag{3.17}$$

- This essentially says that we cannot know precisely both the position and momentum of a particle simultaneously. There is a rigorous definition relating to Fourier transforms, but in short imagine this: If you have a wave with many modes over a long length of string, if someone asks "where" the wave is, you can't give an answer, but you can answer very easily the wavelength (which corresponds to momentum; thanks De Broglie!). However, if you send a single spike through the string, you can very easily tell its position, but cannot give its wavelength. This tradeoff is expressed in Eq. (3.17).

Example 3.1:

A particle of mass m has the wave function:

$$\psi(x,t) = Ax^{-a[(mx^2/\hbar)+it]}. \tag{3.18}$$

a) Find A.

- This is just a matter of normalizing the wavefunction using the familiar relation. It is also helpful to know that we can just set $t = 0$ to normalize, as we proved that the normalization is not time-dependent. So,

$$1 = \int_{-\infty}^{\infty} A^2 e^{-2amx^2/\hbar}\, \mathrm{d}x = 2A^2 \int_0^{\infty} e^{-2amx^2/\hbar}\, \mathrm{d},$$

since the exponential is an even function. From the integral table we know that

$$\int_0^{\infty} x^{2n} e^{-x^2/a^2}\, \mathrm{d}x = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1}. \tag{3.19}$$

Here, we have that $n = 0$, and $a = \sqrt{\hbar/2amx^2}$, so

$$1 = A^2\sqrt{\pi}\sqrt{\frac{\hbar}{2amx^2}},$$

$$\boxed{A = \sqrt[4]{\frac{2am}{\hbar\pi}}}, \tag{3.20}$$

meaning our full, normalized wavefunction is

$$\psi(x,t) = \sqrt[4]{\frac{2am}{\hbar\pi}} e^{-a[(mx^2/\hbar)+it]}. \tag{3.21}$$

b) For what potential $V(x)$ is this a valid solution to the SE?

- We shall just plug this into the SE and solve for $V(x)$:

$$i\hbar\frac{\partial\psi}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi,$$

$$i\hbar(-ai)\psi = -\frac{\hbar^2}{2m}\frac{\partial}{\partial x}\left[-\frac{2amx}{\hbar}\psi\right] + V(x)\psi,$$

$$\hbar a\psi = -\frac{\hbar^2}{2m}\left[-\frac{2am}{\hbar}\psi - \frac{2amx}{\hbar}\psi\left(-\frac{2amx}{\hbar}\right)\right] + V(x)\psi,$$

$$\hbar a = \hbar a - \frac{\hbar^2}{2m}\left(\frac{-2amx}{\hbar}\right)^2 + V(x)\psi,$$

$$\boxed{V(x) = 2ma^2x^2.}$$

c) Calculate $\langle x\rangle$, $\langle x^2\rangle$, $\langle p\rangle$, and $\langle p^2\rangle$.

- Let's start with $\langle x\rangle$:

$$\langle x\rangle = \int_{\infty}^{\infty} x|\psi|^2 \,\mathrm{d}x = \sqrt{\frac{2am}{\hbar\pi}} \int_{-\infty}^{\infty} xe^{-2amx^2/\hbar} \,\mathrm{d}x. \tag{3.22}$$

We can immediately stop here. x is an odd function, and the exponential is an even one. An odd function times an even function gives an odd function, and we are evaluating this function over symmetric intervals, meaning that its zero:

$$\boxed{\langle x\rangle = 0}. \tag{3.23}$$

- Moving to $\langle x^2\rangle$:

$$\langle x^2\rangle = \sqrt{\frac{2am}{\hbar\pi}} \int_{-\infty}^{\infty} x^2 e^{-2amx^2/\hbar} \,\mathrm{d}x = 2\sqrt{\frac{2am}{\hbar\pi}} \int_{0}^{\infty} xe^{-2amx^2/\hbar} \,\mathrm{d}x.$$

We return again to the integral table:

$$\int_0^{\infty} x^{2n} e^{-x^2/a^2} \,\mathrm{d}x = \sqrt{\pi}\frac{(2n)!}{n!}\left(\frac{a}{2}\right)^{2n+1}. \tag{3.24}$$

Here, $n = 1$ and $a = \sqrt{\hbar/2am}$, so:

$$= \left(\frac{2am}{\hbar\pi}\right)^{1/2} \cdot 2 \cdot \sqrt{\pi} \cdot 2 \cdot \left(\frac{\hbar}{2am}\right)^{3/2} = \frac{1}{2}\left(\frac{\hbar}{2am}\right)^{3/2}\left(\frac{2am}{\hbar}\right)^{1/2} = \boxed{\frac{\hbar}{4am}}.$$

- Since $\langle x\rangle = 0$, $\langle p\rangle = 0$ too.
- Lastly, we turn to $\langle p^2\rangle$:

$$\langle p^2\rangle = \int_{-\infty}^{\infty} \psi^* \left(-i\hbar\frac{\partial}{\partial x}\right)^2 \psi \,\mathrm{d}x = -\hbar^2 \int_{-\infty}^{\infty} \psi^* \frac{\partial^2\psi}{\partial x^2} \,\mathrm{d}x.$$

Doing the derivatives:

$$\frac{\partial\psi}{\partial x} = -\frac{2amx}{\hbar}\psi \to \frac{\partial^2\psi}{\partial x^2} = -\frac{2am}{\hbar}\psi + \frac{4a^2m^2x^2}{\hbar^2}\psi.$$

So,

$$\begin{aligned}
\langle p^2\rangle &= -2\hbar^2\sqrt{\frac{2am}{\hbar\pi}} \int_0^{\infty} \left(-\frac{2am}{\hbar} + \frac{4a^2m^2x^2}{\hbar^2}\right) e^{-2amx^2/\hbar} \,\mathrm{d}x, \\
&= 4amh\sqrt{\frac{2am}{\hbar\pi}} \int_0^{\infty} e^{-2amx^2/\hbar} \,\mathrm{d}x - 8a^2m^2\sqrt{\frac{2am}{\hbar\pi}} \int_0^{\infty} x^2 e^{-2amx^2\hbar} \,\mathrm{d}x, \\
&= 4am\hbar\sqrt{\frac{2am}{\hbar\pi}} \cdot \frac{\sqrt{\pi}}{2}\sqrt{\frac{\hbar}{2am}} - 8a^2m^2\sqrt{\frac{2am}{\hbar\pi}} \cdot \frac{2\sqrt{\pi}}{8}\left(\frac{h}{2am}\right)^{3/2}, \\
&= 2am\hbar - 2a^2m^2\left(\frac{h}{2am}\right) = 2am\hbar - am\hbar,
\end{aligned}$$

$$\boxed{\langle p^2\rangle = am\hbar.}$$

d) For σ_x and σ_p; are these consistent with the Heisenberg Uncertainty Principle?

- The definition of the standard deviations is:

$$\sigma_x = \sqrt{\langle x^2 \rangle - \langle x \rangle^2}, \text{ and } \sigma_p = \sqrt{\langle p^2 \rangle - \langle p \rangle^2}. \tag{3.25}$$

  So, for x:

$$\sigma_x = \sqrt{\frac{\hbar}{4am}},$$

  since $\langle x \rangle = 0$. For p:

$$\sigma_p = \sqrt{am\hbar}.$$

  Plugging in:

$$\sqrt{\frac{\hbar}{4am}} \cdot \sqrt{am\hbar} = \frac{\hbar}{2} \geq \frac{\hbar}{2}.$$

- It does indeed satisfy the Heisenberg Uncertainty Principle!

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4 The Time-Independent Schrödinger Equation (TISE)

- Let's recall the ordinary SE, where we will write the wavefunction now as capital Ψ.

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V\Psi. \tag{4.1}$$

- Now that we have explored the properties of this equation, we are now interested in what solutions to it might look like. As a PDE, our first move as physicists should be *separation of variables*. Let's assume a solution like $\Psi(x,t) = \phi(t)\psi(x)$, and plug it in:

$$i\hbar\psi \frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\phi \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\phi\psi. \tag{4.2}$$

- Dividing both sides by $\phi\psi$, we get

$$i\hbar \frac{1}{\phi}\frac{\mathrm{d}\phi}{\mathrm{d}t} = -\frac{\hbar^2}{2m}\frac{1}{\psi}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V. \tag{4.3}$$

- Now, since we have two completely independent quantities on either side, they must be equal to a constant, which we will call E (this will be identified as the energy):

$$\begin{cases} \dfrac{\mathrm{d}\phi}{\mathrm{d}t} = -\dfrac{iE}{\hbar}\phi, \\ -\dfrac{\hbar^2}{2m}\dfrac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + V\psi = E\psi. \end{cases} \tag{4.4}$$

- The t equation is super simple:

$$\phi(t) = e^{-iEt/\hbar}, \tag{4.5}$$

  where we have just chosen to absorb the constant into ψ.

- The x equation is unsolvable until we know what our potential V is; Eq. (4.4) is the **time-independent Schrödinger Equation (TISE)**.

- Upon further examination, we can identify it with the Hamiltonian operator we found earlier:

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2} + V, \tag{4.6}$$

so the TISE becomes

$$\hat{H}\psi = E\psi, \tag{4.7}$$

or an eigenvalue equation.

- To motivate why we'd be interested in such solutions, since it seems unlikely that such a wild assumption from the beginning can provide any sort of meaninful results, we can make the following observations: first, these are *stationary* states. Now, the probability density is time-independent, as we saw before, and so are our expectation values. Let's show the latter:

$$\langle x \rangle = \langle \Psi | \, x \, | \Psi \rangle = \int \Psi^* x \Psi \, \mathrm{d}x = \int e^{iEt/\hbar} \psi x e^{-iEt/\hbar} \psi \, \mathrm{d}x = \int \psi^* x \psi \, \mathrm{d}x. \tag{4.8}$$

- The same will be true for the other expectation values that we have looked at thus far. So, when looking at these values, we might as well just drop the time-dependent factor and only focus on the time-independent solutions to determine these values. Hence, these TISE solutions, since they are easier to solve for, are useful in that regard.
- Additionally, we have that such solutions, upon measurement, give a definite value for the energy, i.e. $\sigma_H = 0$. To show this, let's calculate $\langle \hat{H} \rangle$ and $\langle \hat{H} \rangle$:

$$\langle \hat{H} \rangle = \int \psi^* \hat{H} \psi \, \mathrm{d}x, \tag{4.9}$$

but from the TISE, we know that $\hat{H}\psi = E\psi$, so

$$\langle \hat{H} \rangle = E \int \psi^* \psi \, \mathrm{d}x = E \int |\psi|^2 \, \mathrm{d}x = E. \tag{4.10}$$

- Next, we have that

$$\hat{H}^2 \psi = \hat{H}\left(\hat{H}\psi\right) = E\left(\hat{H}\psi\right) = E^2 \psi, \tag{4.11}$$

- So,

$$\langle \hat{H}^2 \rangle = \int \psi^* \hat{H}^2 \psi \, \mathrm{d}x = E^2 \int \psi^* \psi \, \mathrm{d}x = E^2. \tag{4.12}$$

- Therefore,

$$\sigma_H = \sqrt{\langle \hat{H}^2 \rangle - \langle \hat{H} \rangle^2} = \sqrt{E^2 - E^2} = 0. \tag{4.13}$$

- Hence, we have shown that there is zero variance in the value of E resulting from the Hamiltonian operator, meaning that the energy is the same for every measurement.
- Additionally, it can be shown that when solving for the TISE, we actually get an infinite number of solutions corresponding to the infinite number of possible definite energy states. Further, since the SE is linear, the sum of all of these solutions is equal to the full, general solution. More formally, the nth solution is given by

$$\Psi_n(x,t) = \psi_n(x) e^{-iE_n t/\hbar}, \tag{4.14}$$

so the full solution would be:

$$\Psi(x,t) = \sum_n c_n \psi_n(x) e^{-iE_n t/\hbar} = \sum_n c_n \Psi_n(x,t), \tag{4.15}$$

where the c_n's are constants. For $t = 0$, when one is looking to normalize the wavefunction, this reduces to

$$\Psi(x,0) = \sum_n c_n \psi_n(x). \tag{4.16}$$

Example 4.1:

Prove the following statement: For normalizable solutions, E must be real.

- First, let's start by assuming $E = E_0 + iE_1$. Then, our general solution becomes:

$$\Psi = A\psi e^{-i(E_0+iE_1)t/\hbar} = A\psi e^{-iE_0t/\hbar} \cdot e^{E_1t/\hbar}. \tag{4.17}$$

Let's normalize this:

$$\int |\Psi|^2 \, \mathrm{d}x = A^2 \int \psi^* \psi e^{-iE_0t/\hbar} e^{iE_0t/\hbar} \cdot e^{E_1t/\hbar} \cdot e^{E_1t/\hbar} \, \mathrm{d}x \tag{4.18}$$

$$= A^2 e^{2E_1t/\hbar} \int |\psi|^2 \, \mathrm{d}x \tag{4.19}$$

$$= A^2 e^{2E_1t/\hbar} = 1. \tag{4.20}$$

Now, we have already proved that a function normalized at one particular time stays normalized for all other times. However, here we have a time-dependent term equalling a constant. Therefore, for our function to be able to be normalized, we must have $E_1 = 0$ to remove the time-dependent term. E_1 was the imaginary term, hence, the separation constant cannot be imaginary.

The Infinite Square Well

- With some of the formalism out of the way we can start looking at solving some specific examples using the TISE. The first of these is the infinite square well, in which a particle is confined to some region (a "well") by an infinite potential on either side. In this particular example, we imagine a potential

$$V = \begin{cases} 0, & 0 \leq x \leq a, \\ \infty & \text{elsewhere.} \end{cases}$$

- Notably, this is not time-dependent, meaning we can use the TISE. Now, since the potential is infinite outside the well, there is zero chance the particle could end up there, so $\psi = 0$ outside. Inside, we have a zero potential, so the TISE reduces to:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi.$$

Rewriting:

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2mE}{\hbar^2}\psi = 0,$$

or, defining

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

we can write this as

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + k^2\psi = 0.$$

- However, negative energy states are possible, right? In this case, actually, this is not the case, and it is a small exercise to show that for a normalizable stationary state, the minimum allowed energy must exceed the potential. Let's show this, since its easy.

- We first rewrite the TISE like so:
$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = \frac{2m}{\hbar^2}\left[V(x) - E\right]\psi.$$
Let's consider when $E < V$. In this case, we have that both the wavefunction and its second derivative are of the same sign. So, if our wavefunction itself is positive, then the second derivative must be positive. A positive function with a positive second derivative means that it will be curving up away from the x-axis, getting larger and larger, and vice versa for a negative wavefunction. So, in either case, the wavefunction either increases to infinity or decreases to infinity. The only other way for this not to be the case is if the wavefunction is zero, but that also is not normalizable.

- Now that we have shown that, we can more safely place the energy within the square root as shown above.

- The solutions to our TISE for the infinite square well are just sines and cosines:
$$\psi(x) = A\cos(kx) + B\sin(kx).$$
We now just quote results from future chapters, the main one being that the wavefunction must be continuous. This seems intuitive, but it'll be proved later supposedly. Due to this, the wavefunction at the end points of the well must be zero:
$$\psi(0) = A\cos 0 + B\sin 0 = A = 0,$$
so we have eliminated the cos part and just have
$$\psi(x) = A\sin(kx),$$
where I have just relabeled the constant to be A.

- Next, we apply the other boundary condition:
$$\psi(a) = A\sin(ka) = 0.$$
Here, though, we can either set $A = 0$ or $\sin(ka) = 0$. We don't want to do $A = 0$, the trivial solution, because such a wavefunction, as just mentioned, is not normalizable. So, we must set $\sin(ka) = 0$. This means that the quantity ka must be an integer multiple of π (and cannot be zero!):
$$ka = n\pi \;\rightarrow\; k = \frac{n\pi}{a}.$$

- But wait... Recalling how we defined k in the first place:
$$\begin{aligned}
\frac{n\pi}{a} &= \frac{\sqrt{2mE}}{\hbar}, \\
\frac{n^2\pi^2}{a^2} &= \frac{2mE}{\hbar^2}, \\
\rightarrow \boxed{E &= \frac{n^2\pi^2\hbar^2}{2ma}.}
\end{aligned}$$

- What we have just shown is that the energy values for this system can only take on discrete values, as dictated by the n^2! This is extremely unexpected from a classical standpoint.

- Now back to our wavefunction, we can now normalize to determine A:

$$\begin{aligned} A^2 \int_0^a \sin^2(kx)\,\mathrm{d}x &= \frac{A^2}{2}\int_0^a (1-\cos(2kx))\,\mathrm{d}x, \\ &= \frac{A^2}{2}\left[x - \frac{1}{2k}\sin(kx)\right]_0^a, \\ &= \frac{A^2}{2}\left[a - \frac{2a}{n\pi}\sin(2n\pi)\right], \\ &= \frac{A^2 a}{2} = 1, \\ \rightarrow \boxed{A = \sqrt{\frac{2}{a}}.} \end{aligned}$$

  Our wavefunction is, therefore:

$$\psi_n(x) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), \tag{4.21}$$

  where I have added the subscript n to signify that we now have an infinite set of discretized solutions.

- We can now quote a couple of properties about our infinite set of solutions and the TISE in general:

  1. Our set of solutions alternate between even and odd. For instance, ψ_1 is even, ψ_2 is odd, ψ_3 is even again, and so on.
  2. Each successive increase in energy adds one node to the resulting plots of the energy. A node is basically a crossing of the x-axis by the wave.
  3. They are mutually orthogonal to each other, meaning that

$$\int \psi_i(x)^* \psi_j(x)\,\mathrm{d}x = \delta_{ij}. \tag{4.22}$$

     This captures that when $i = j$, the wavefunctions are the same and it is just the normalization condition, but if $i \neq j$, then the result is zero. This is the definition of orthogonality, and it means that the set itself is **orthonormal**.
  4. The set is **complete**, meaning that we can express any function $f(x)$ by using our solutions in a linear combination:

$$f(x) = \sum_n c_n \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right).$$

     This shouldn't be shocking, since we have basically just constructed a Fourier series, and we know from **Dirichlet's Theorem** that we can represent any function as a Fourier series.

- Lastly, we can assemble the full time-dependent solutions by tacking on the exponential time factor:

$$\Psi_n(x,t) = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.$$

  And, again, the most general solution is a linear combination, so:

$$\boxed{\Psi(x,t) = \sqrt{\frac{2}{a}}\sum_n c_n \sin\left(\frac{n\pi x}{a}\right) e^{-i(n^2\pi^2\hbar/2ma^2)t}.} \tag{4.23}$$

- The general way to solve a problem using this, is to take the given initial wavefunction $\Psi(x,0)$, then from the completeness of the ψ_n's, we can use our initial wavefunction to find the c_n's using Fourier's trick:

$$c_n = \int \psi_n^\dagger(x)\Psi(x,0)\,\mathrm{d}x, \tag{4.24}$$

and from there, we can assemble the full solution using Eq. (4.23).

Example 4.2:

Before moving on to more series examples, let's first explore further our solutions to this infinte square well. Let's calculate the expectation values of x, x^2, p, and p^2 along with their uncertainties for the nth state.

- Since the expectation values are time-independent (either way, the time-dependent exponential cancels), we can just do:

$$\begin{aligned}
\langle x\rangle &= \int \psi_n^* x\psi\,\mathrm{d}x = \frac{2}{a}\int_0^a x\sin^2\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x,\\
&= \frac{1}{a}\int_0^a x\left[1-\cos\left(\frac{2n\pi x}{a}\right)\right]\,\mathrm{d}x,\\
&= \frac{1}{a}\int_0^a x\,\mathrm{d}x - \frac{1}{a}\int_0^a x\cos\left(\frac{2n\pi x}{a}\right)\,\mathrm{d}x,\\
&= \frac{a}{2} - \frac{1}{a}\left\{\frac{xa}{2n\pi}\sin\left(\frac{2n\pi x}{a}\right)\Big|_0^a - \frac{a}{2n\pi}\int_0^a \sin\left(\frac{2n\pi x}{a}\right)\,\mathrm{d}x\right\}.
\end{aligned}$$

The first term in the braces vanishes, so we have

$$\begin{aligned}
\langle x^2\rangle &= \frac{a}{2} - \frac{1}{a}\left[\frac{a^2}{4n^2\pi^2}\cos\left(\frac{2n\pi x}{a}\right)\right]_0^a,\\
&= \frac{a}{2} - \frac{a}{4n^2\pi^2}\left[\cos(2n\pi)-1\right].
\end{aligned}$$

Cosine of an integer multiple of 2π is always 1, so the entire term with brackets vanishes, leaving:

$$\langle x\rangle = \frac{a}{2}.$$

- Since we got this from the full time-dependent equation we can say

$$\langle p\rangle = \frac{\mathrm{d}\langle x\rangle}{\mathrm{d}t} = 0.$$

- Now,

$$\begin{aligned}
\langle x^2\rangle &= \frac{1}{a}\int_0^a x^2\,\mathrm{d}x - \frac{1}{a}\int_0^a x^2\cos\left(\frac{2\pi x}{a}\right)\,\mathrm{d}x,\\
&= \frac{a^2}{3} + \frac{1}{a}\left\{\frac{ax^2}{2n\pi}\sin\left(\frac{2n\pi x}{a}\right)\Big|_0^a - \frac{a}{n\pi}\int_0^a x\sin\left(\frac{2n\pi x}{a}\right)\,\mathrm{d}x\right\}.
\end{aligned}$$

Again, the first term in braces vanishes;

$$\begin{aligned}
\langle x^2\rangle &= \frac{a^2}{3} + \frac{1}{n\pi}\int_0^a x\sin\left(\frac{2n\pi x}{a}\right)_0^a\,\mathrm{d}x,\\
&= \frac{a^2}{3} + \frac{1}{n\pi}\left\{-\frac{xa}{2n\pi}\cos\left(\frac{2n\pi x}{a}\right)\Big|_0^a - \frac{a}{2n\pi}\int_0^a \cos\left(\frac{2n\pi x}{a}\right)\,\mathrm{d}x\right\}.
\end{aligned}$$

The integral will give a sine, evaluated over the same limits as before, and will vanish. So

$$\begin{aligned}\langle x^2\rangle &= \frac{a^2}{3} + \frac{1}{n\pi}\left(\frac{-a^2}{2n\pi}\right),\\ &= \frac{a^2}{3} - \frac{a^2}{2n^2\pi^2},\\ \langle x^2\rangle &= a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right).\end{aligned}$$

- Next,

$$\begin{aligned}\langle p^2\rangle &= \int \psi_n^*(x)\left(-i\hbar\frac{\mathrm{d}^2}{\mathrm{d}x^2}\right)^2\psi_n(x)\,\mathrm{d}x,\\ &= -\hbar^2\int \psi_n^*(x)\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x.\end{aligned}$$

From our TISE, we know that

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi = -\frac{2mE}{\hbar^2}\psi = -\frac{2m}{\hbar^2}\left(\frac{n^2\pi^2\hbar^2}{2ma^2}\right)\psi = -\frac{n^2\pi^2}{a},$$

so

$$\langle p^2\rangle = \frac{n^2\pi^2\hbar^2}{a^2}\int |\psi_n|^2\,\mathrm{d}x = \frac{n^2\pi^2\hbar^2}{a^2}.$$

- Next,

$$\begin{aligned}\sigma_x &= \sqrt{a^2\left(\frac{1}{3} - \frac{1}{2n^2\pi^2}\right) - \left(\frac{a}{2}\right)^2},\\ \sigma_p &= \sqrt{\frac{n^2\pi^2\hbar^2}{a^2}} = \frac{n\pi\hbar}{a}.\end{aligned}$$

Putting them into the uncertainty relation:

$$\begin{aligned}\sigma_x\sigma_p &= \hbar\sqrt{\frac{\pi^2n^2}{3} - \frac{1}{2} - \frac{n^2\pi^2}{4}},\\ &= \frac{\hbar}{2}\sqrt{\frac{4\pi^2n^2}{3} - 2 - n^2\pi^2},\\ &= \frac{\hbar}{2}\sqrt{\frac{n^2\pi^2}{3} - 2} \geq \frac{\hbar}{2}.\end{aligned}$$

This is satisfied since $\pi^2/3 > 3$, and $n^2 > 1$, so $n^2\pi^2/3 > 2$ always.

- The value of n that brings this closest to the limit is actually the smallest and most likely value, $n = 1$. Larger values make the value in the square root larger, so the smallest possible value is the right one.

Example 4.3:

A particle in an infinite square well has the initial wave function

$$\Psi(x,0) = \begin{cases} Ax & 0 \leq x \leq a/2,\\ A(a-x) & a/2 \leq x \leq a.\end{cases} \tag{4.25}$$

Find A, then find $\Psi(x,t)$.

- First, we just normalize the wave function to find A:

$$\begin{aligned}
\langle\psi|\psi\rangle &= A^2\int_0^{a/2} x^2\,\mathrm{d}x + A^2\int_{a/2}^{a}(a-x)^2\,\mathrm{d}x,\\
&= A^2\left[\frac{1}{2}\left(\frac{a}{2}\right)^3 + \int_{a/2}^{a} x^2\,\mathrm{d}x - 2a\int_{a/2}^{a} x\,\mathrm{d}x + a^2\int_{a/2}^{a}\,\mathrm{d}x\right],\\
&= A^2\left\{\frac{a^3}{24} + \frac{1}{3}\left[a^3 - \left(\frac{a}{2}\right)^3\right] - a\left[a^2 - \left(\frac{a}{2}\right)^2\right] + a^2\left(a - \frac{a}{2}\right)\right\},\\
&= A^2\left[\frac{a^3}{24} + \frac{a^3}{3}\left(\frac{7}{8}\right) - a^3\left(\frac{3}{4}\right) + a^3\left(\frac{1}{2}\right)\right],\\
&= A^2a^3\left(\frac{1}{3} - \frac{3}{4} + \frac{1}{2}\right) = A^2a^3\left(\frac{4}{12} - \frac{9}{12} + \frac{6}{12}\right) = \frac{A^2a^3}{12} = 1,
\end{aligned}$$

so

$$\boxed{A = \sqrt{\frac{12}{a^3}}.}$$

- To find the general solution, we can use Eq. (4.24) and substitute ψ_n with Eq. (4.21) and $\Psi(x,0)$ with our given wavefunction:

$$c_n = \sqrt{\frac{2}{a}}\sqrt{\frac{12}{a^3}}\left[\int_0^{a/2} x\sin\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x + \int_{a/2}^{a}(a-x)\sin\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x\right].$$

Looking at the first integral first:

$$\begin{aligned}
\int_0^{a/2} x\sin\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x &= \left[-\frac{xa}{n\pi}\cos\left(\frac{n\pi x}{a}\right)\right]_0^{a/2} + \frac{a}{n\pi}\int_0^{a/2}\cos\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x,\\
&= -\frac{a^2}{2n\pi}\cos\left(\frac{n\pi}{2}\right) + \frac{a^2}{n^2\pi^2}\sin\left(\frac{n\pi}{2}\right).
\end{aligned}$$

Now for the second integal:

$$\int_{a/2}^{a}(a-x)\sin\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x = a\int_{a/2}^{a}\sin\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x - \int_{a/2}^{a} x\sin\left(\frac{n\pi x}{a}\right)\,\mathrm{d}x,$$

$$\begin{aligned}
&= \left[-\frac{a^2}{n\pi}\cos\left(\frac{n\pi x}{a}\right)\right]_{a/2}^{a} - \left[-\frac{xa}{n\pi}\cos\left(\frac{n\pi x}{a}\right)\right]_{a/2}^{a} + \left[\frac{a^2}{n^2\pi^2}\sin\left(\frac{n\pi x}{a}\right)\right]_{a/2}^{a},\\
&= -\frac{a^2}{n\pi}\left[\cos(n\pi) - \cos\left(\frac{n\pi}{2}\right)\right] + \frac{a}{n\pi}\left[a\cos(n\pi) - \frac{a}{2}\cos(\frac{n\pi}{2})\right] - \frac{a^2}{n^2\pi^2}\left[\sin(n\pi) - \sin\left(\frac{n\pi}{2}\right)\right],\\
&= \frac{a^2}{2n\pi}\cos\left(\frac{n\pi}{2}\right) + \frac{a^2}{n^2\pi^2}\sin\left(\frac{n\pi}{2}\right).
\end{aligned}$$

Adding the two together,

$$\begin{aligned}
c_n &= \sqrt{\frac{24}{a^4}}\left[-\frac{a^2}{2n\pi}\cos\left(\frac{n\pi}{2}\right) + \frac{a^2}{n^2\pi^2}\sin\left(\frac{n\pi}{2}\right) + \frac{a^2}{2n\pi}\cos\left(\frac{n\pi}{2}\right) + \frac{a^2}{n^2\pi^2}\sin\left(\frac{n\pi}{2}\right)\right],\\
&= \frac{4\sqrt{6}}{n^2\pi^2}\sin\left(\frac{n\pi}{2}\right),\\
&= \begin{cases} \frac{(-1)^{(n-1)/2}4\sqrt{6}}{n^2\pi^2} & \text{odd } n,\\ 0 & \text{even } n. \end{cases}
\end{aligned}$$

At last, then, our general solution is

$$\boxed{\Psi(x,t) = \frac{4\sqrt{6}}{\pi^2} \sum_{n=1,3,5,\ldots}^{\infty} \frac{(-1)^{(n-1)/2}}{n^2} \sin\left(\frac{n\pi x}{a}\right) e^{-i(n^2\pi^2\hbar)t/(2ma^2)}.}$$

Now, what is the probability that a measurement of the energy will yield E_1?

- We know that the probability of measuring state n is $|c_n|^2$:

$$P(E = E_1) = \left(\frac{(-1)^{(1-1)/2} 4\sqrt{6}}{1^2\pi^2}\right)^2 = \frac{96}{\pi^4} \approx 0.9855.$$

Lastly, find $\langle H \rangle$, using the formula

$$\langle H \rangle = \sum_{n=1}^{\infty} |c_n|^2 E_n. \tag{4.26}$$

- Let's just plug in:

$$\langle H \rangle = \sum_{n=1,3,5,\ldots}^{\infty} \left(\frac{(-1)^{(n-1)/2} 4\sqrt{6}}{n^2\pi^2}\right)^2 \left(\frac{n^2\pi^2\hbar^2}{2ma^2}\right) = \frac{48\hbar}{ma^2\pi^2} \sum_{n=1,3,5,\ldots}^{\infty} \frac{1}{n^2}.$$

The infinite series turns out to be $\pi^2/8$, so the expectation value for the energy is:

$$\boxed{\langle H \rangle = \frac{6\hbar^2}{ma^2}.}$$

The Simple Harmonic Oscillator

- The **simple harmonic oscillator** (SHO) involves a force acting on a particle that is directly and oppositely proportional to its distance from some equilibrium position:

$$F \propto -x.$$

If we call the proportionality constant k, we have *Hooke's Law*:

$$\begin{aligned} F &= -kx, \\ m\frac{\mathrm{d}^2x}{\mathrm{d}t^2} &= -kx, \\ \frac{\partial^2 x}{\partial t^2} + \frac{k}{m}x &= 0, \\ \frac{\partial^2 x}{\partial t^2} + \omega^2 x &= 0, \end{aligned}$$

where $\omega = \sqrt{k/m}$.

- Solutions to this equation are waves.

- Now we know that for conservative forces, $F_x = -\boldsymbol{\nabla}_x V$, or $V = -\int F \, \mathrm{d}x$. Thus,

$$V = \int kx \, \mathrm{d}x = \frac{1}{2} m\omega^2 x^2.$$

- Bringing this to a quantum system, we note that this potential is time-independent, meaning we can apply the TISE:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{1}{2}m\omega^2 x^2 \psi = E\psi.$$

- This is super tricky to solve, so we will use an ad hoc solution that people a long time ago found the hard way. The first step in this clever method is to write our TISE like so:

$$\frac{1}{2m}\left[-\hbar^2\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + m^2\omega^2 x^2 \psi\right] = E\psi,$$
$$\frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 + (m\omega x)^2\right]\psi = E\psi.$$

  Now let's define

$$\hat{a}_\pm = \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x} \pm im\omega x\right), \tag{4.27}$$

- Ordinarily we could factor our TISE simply into $\hat{a}_\pm$, but since $\hat{a}$ is an operator, it is not so simple. Let's examine these operators using a test function $f(x)$. First,

$$\begin{aligned}\hat{a}_-\hat{a}_+ f(x) &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right) - im\omega x\right]\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right) + im\omega x\right] f(x), \\ &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 f(x) + \hbar m\omega\frac{\mathrm{d}}{\mathrm{d}x}[xf(x)] - \hbar m\omega x\frac{\mathrm{d}}{\mathrm{d}x}[f(x)] + (m\omega x)^2 f(x)\right].\end{aligned}$$

  We need the product rule for the second term. We can see that we will end up with a term identical to the third term but positive, so those cancel, meaning all we are left with is a term that has $\mathrm{d}x/\mathrm{d}x$, which is 1:

$$\begin{aligned}\hat{a}_-\hat{a}_+ f(x) &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 f(x) + (m\omega x)^2 f(x) + \hbar m\omega f(x)\right], \\ &= \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 + (m\omega x)^2 + \hbar m\omega\right] f(x).\end{aligned}$$

  We can now drop the test function and move some things around to get:

$$\hat{a}_-\hat{a}_+ = \frac{1}{2m}\left[\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x}\right)^2 + (m\omega x)^2\right] + \frac{1}{2}\hbar\omega.$$

  Or, using the definition of the momentum operator $\hat{p} = -i\hbar\mathrm{d}/\mathrm{d}x$:

$$\hat{a}_-\hat{a}_+ = \frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right] + \frac{1}{2}\hbar\omega. \tag{4.28}$$

  We can find similarly that

$$\hat{a}_+\hat{a}_- = \frac{1}{2m}\left[\hat{p}^2 + (m\omega x)^2\right] - \frac{1}{2}\hbar\omega.. \tag{4.29}$$

- It is important to note that these do not commute! That is, $[\hat{a}_-, \hat{a}_+] \neq 0$. The non-commutability of operators is something we will examine a little more later, but it is a stable of quantum mechanics.

- We can also note that the term in brackets is identical to that in our TISE, so we can write (dropping the hats on the a's for simplicity; they are still operators)

$$\left(a_- a_+ - \frac{1}{2}\hbar\omega\right)\psi = E\psi, \quad \text{or} \quad \left(a_+ a_- + \frac{1}{2}\hbar\omega\right)\psi = E\psi$$

- Here is the big claim, and the reason why we defined these strange operators: *If ψ is a solution to the TISE with energy E, then so too is $a_+\psi$ with energy $E + \hbar\omega$.* What we have found, then, is a systematic way to go from one solution to the infinite other solutions! One may not want to actually compute all of them manually this way, but nevertheless, we now have a way to go from one solution to many others. To prove this:

$$\begin{aligned}
\hat{H}a_+ |\psi\rangle &= (a_+ a_- + \frac{1}{2}\hbar\omega)a_+ |\psi\rangle = (a_+ a_- a_+ + \frac{1}{2}\hbar\omega a_+) |\psi\rangle , \\
&= a_+(a_- a_+ + \frac{1}{2}\hbar\omega) |\psi\rangle = a_+(a_- a_+ - \frac{1}{2}\hbar\omega + \hbar\omega) |\psi\rangle , \\
&= a_+(\hat{H} + \hbar\omega) |\psi\rangle = a_+(E + \hbar\omega) |\psi\rangle , \\
&= (E + \hbar\omega)a_+ |\psi\rangle .
\end{aligned}$$

- We can find similarly that $\hat{H}a_- |\psi\rangle - (E - \hbar\omega)a_- |\psi\rangle$.
- These operators are therefore called the **ladder operators** or **raising and lowering operators**.
- However, nothing prevents us from applying the lowering operator infinitely, but we know from before that the energy cannot go below the minimum value of the potential. Hence, there must some wavefunction ψ_0 such that when we apply the lowering operator, we get zero: $a_- |\psi_0\rangle = 0$:

$$a_- |\psi_0\rangle = \frac{1}{\sqrt{2m}}\left(\frac{\hbar}{i}\frac{\mathrm{d}}{\mathrm{d}x} - im\omega x\right)\psi_0 = 0,$$

$$\begin{aligned}
\frac{\hbar}{i}\frac{\mathrm{d}\psi_0}{\mathrm{d}x} &= im\omega x\psi_0, \\
\frac{\mathrm{d}\psi_0}{\mathrm{d}x} &= -\frac{m\omega x}{\hbar}\psi_0, \\
\int \frac{\mathrm{d}\psi_0}{\psi_0} &= -\frac{m\omega}{\hbar}\int x\ \mathrm{d}x, \\
\ln\psi_0 &= \frac{m\omega x^2}{2\hbar}, \\
\boxed{\psi_0 &= \exp\left(-\frac{m\omega x^2}{2\hbar}\right).}
\end{aligned}$$

- Now we should normalize it by sticking a constant in front: $\psi_0 \to A_0 \exp\left(-\frac{m\omega x^2}{2\hbar}\right)$:

$$\begin{aligned}
\langle\psi_0 \,|\, \psi_0\rangle &= A_0^2 \int \exp\left(-\frac{m\omega x^2}{\hbar}\right)\ \mathrm{d}x, \\
&= A_0^2\sqrt{\frac{\pi\hbar}{m\omega}} \cdot \frac{1}{2} = 1,
\end{aligned}$$

so

$$A_0 = \sqrt[4]{\frac{4m\omega}{\pi\hbar}}.$$

Thus,

$$\boxed{\psi_0 = \sqrt[4]{\frac{4m\omega}{\pi\hbar}}\exp\left(-\frac{m\omega x^2}{2\hbar}\right).}$$

- This is the ground state for the simple harmonic oscillator, and we can now apply the raising operator as many times as we want to determine higher energy states. For instance, $|\psi_1\rangle = A_1 a_+ |\psi_0\rangle$, where A_1 is another constant we need to find. Generally,

$$\boxed{|\psi_n\rangle = A_n (a_+)^n |\psi_0\rangle ,} \tag{4.30}$$

or, it can be shown that we can find the coefficients algebraically:

$$\boxed{|\psi_n\rangle = \frac{1}{\sqrt{n!}} (a_+)^n |\psi_0\rangle .} \tag{4.31}$$

The Free Particle

- Let's now turn our attention to a free particle that is subject to no potential anywhere. The TISE then is just

$$\begin{aligned} -\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} &= E\psi, \\ \rightarrow \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + \frac{2mE}{\hbar}\psi &= 0, \end{aligned}$$

or, letting $k \equiv 2mE/\hbar$ just like before, we get

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} + k^2\psi = 0.$$

This has solutions that are plane-waves, and we will write them in exponential form this time:

$$\psi(x) = Ae^{ikx} + Be^{-ikx},$$

where $\mathbf{k}$ is the wave-number, associated with the momentum through De Broglie's relation of $\mathbf{p} = \hbar\mathbf{k}$. Tacking on the time-dependent part:

$$\Psi(x,t) = Ae^{ik(x-\frac{\hbar k}{2m}t)} + Be^{-ik(x+\frac{\hbar k}{2m}t)}, \tag{4.32}$$

or, since the two terms differ only by the sign of k, we can just let k run negative as well and say

$$\Psi(x,t) = Ae^{i(kx-\frac{\hbar k^2}{2m}t)}.$$

- The problem here though is that we don't have boundary conditions to restrict anything, so we have no way forward with methods that we have used before. The even more disastrous problem is that this is not normalizable:

$$\langle \Psi \,|\, \Psi \rangle = A^2 \int_{-\infty}^{\infty} \mathrm{d}x.$$

- What this means is that these are not physically realizable states. Or, since the TISE is the energy/Hamiltonian eigenvalue equation, the plane-wave solutions do not have definite energy.

- However, despite this, these plane-wave solutions still serve a purpose: the idea we introduced before that the general solution is a linear combination of all the stationary states is still very much valid. This time, though, we don't have any relations to discretize k, so in the continuum limit, we have an integral rather than a sum:

$$\Psi(x,t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{i\left(kx-\frac{\hbar k^2}{2m}t\right)} \,\mathrm{d}k. \tag{4.33}$$

The factor of $1/\sqrt{2\pi}$ is there because this is *almost* a Fourier transform.

- Now, in most problems, we will be given some initial wavefunction $\Psi(x,0)$, so that Eq. (4.33) becomes

$$\Psi(x,0) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \phi(k) e^{ikx} \, \mathrm{d}k. \tag{4.34}$$

  This time, it doesn't just *look* like the Fourier transform, it is! This means that it is particularly easy to find the Fourier inverse $\phi(k)$:

$$\phi(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \Psi(x,0) e^{-ikx} \, \mathrm{d}x \tag{4.35}$$

Example 4.4:

A free particle is initially localized in the range $-a < x < a$, then is "released" at $t = 0$, where $\Psi(x,0) = A$ in this range, and zero otherwise.

- First, since the particle is initially localized in that range, we are able to integrate:

$$\langle \Psi \mid \Psi \rangle = A^2 \int_{-a}^{a} = 2aA^2 = 1 \;\rightarrow\; \boxed{A = \sqrt{\frac{1}{2a}}.}$$

- Now we need to find the coefficient $\phi(k)$:

$$\begin{aligned} \phi(k) &= \frac{1}{2\sqrt{\pi a}} \int_{-a}^{a} e^{-ikx} \, \mathrm{d}x, \\ &= \frac{1}{k\sqrt{\pi a}} \left(\frac{e^{ika} - e^{-ika}}{2i} \right), \\ &= \frac{\sin(ka)}{k\sqrt{\pi a}}. \end{aligned}$$

- So, the final solution is

$$\boxed{\Psi(x,t) = \frac{1}{\pi\sqrt{2a}} \int_{-a}^{a} \frac{\sin(ka)}{k} e^{i\left(kx - \frac{\hbar k^2}{2m} t\right)}.}$$

Bound and Scattering States

- Really quickly a discussion on bound vs. scattering states. Classically, if a particle's total energy is less than the potential, then the potential acts as a well, keeping the particle contained in whatever way, since the particle can never just spuriously gain energy in order to escape.
- On the other hand, a particle may be able to come in from the left (imagine a Gaussian sort of distribution as the potential), but it may have enough energy to get up and all the way over the hill, so it escapes to the right.
- The former case is called a **bound state**, and the latter is called a **scattering state**. Now, we will find soon that a quantum particle has a non-zero probability to tunnel through any potential wall, so long as it isn't infinite. So, what we are really considering is the limits as $x \to \pm\infty$. Generalizing the previous qualitative results, then, we can say

$$\begin{cases} E < (V(-\infty) \text{ and } V(+\infty)) & \Rightarrow \text{boundstate}, \\ E > (V(-\infty) \text{ and } V(+\infty)) & \Rightarrow \text{scatteringstate}, \end{cases}$$

- Thus, since the infinite square well has a potential that goes to infinity at the limits, it forms only bound states; this is also the case for the simple harmonic oscillator. Since the free particle has no potential anywhere, it forms scattering states (the free particle being differentiated from the bound states is related to why its stationary states aren't themselves normalizable/physically realizable, and why we had to do different stuff with it).

The Delta-Function Well

- I already know about the delta function, so I won't write about it here. We will now consider a potential of the form $V(x) = -\alpha\delta(x)$, where α is some real, positive constant. Now, since we have $\delta(\pm\infty)$, we can form either bound states with $E < 0$ or scattering states with $E > 0$.

- Doing the usual shenanigans, we first consider the region $x < 0$. The potential there is zero, so we have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi.$$

  Rearranging, we get

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = k^2\psi,$$

  where $k \equiv \sqrt{-2mE}/\hbar$. This has real exponential solutions:

$$\psi(x) = Ae^{-kx} + Be^{kx}.$$

  Since we are considering the region $x < 0$, we have the boundary condition where $x \to -\infty$. In such a case, the A term blows up, so we disregard it:

$$\psi(x) = Be^{kx}, \quad \text{for } x < 0.$$

  Similarly, we find

$$\psi(x) = Ae^{-kx} \quad \text{for } x > 0.$$

- We obviously want ψ to be continuous, so in order for this to be the case, both equations must be equal to each other at $x = 0$. This means that $A = B$:

$$\begin{cases} \psi(x) = Ae^{kx} & \text{for } x < 0, \\ \psi(x) = Ae^{-kx} & \text{for } x > 0. \end{cases}$$

- Now we need something else to determine B and k. Ordinarily, we'd impose continuity of the first derivative, but as we are about to show, this doesn't quite work for potentials like the delta function (it isn't even really a function, anyways, so that should immediately hint at something not working quite right).

- First, let's just integrate the TISE over the range $[-\epsilon, \epsilon]$, and then take $\epsilon \to \infty$:

$$-\frac{\hbar^2}{2m}\int_{-\epsilon}^{\epsilon}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2}\,\mathrm{d}x + \int_{-\epsilon}^{\epsilon}V(x)\psi(x)\,\mathrm{d}x = E\int_{-\epsilon}^{\epsilon}\psi(x)\,\mathrm{d}x.$$

  Now, the first term just cancels one of the derivatives, and the final term on the right is just zero in the limit of $\epsilon \to 0$, since ψ *has* to be well-behaved by construction, so it should vanish under such an integral. $V(x)$ is weird tho, so let's go a bit further first. We now have

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) \equiv \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{+\epsilon} - \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-\epsilon} = \frac{2m}{\hbar^2}\int_{-\epsilon}^{\epsilon}V(x)\psi(x)\,\mathrm{d}x.$$

where $\Delta(f(x))$ is a measure of continuity. *Ordinarily*, for any *real* potential, the right-hand integral will also be zero, and thus the first derivative will be continuous, but this is not the case here as the potential is infinite in the integral limits. Specifically,

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = -\frac{2m\alpha}{\hbar^2}\int_{-\epsilon}^{\epsilon}\delta(x)\psi(x)\,\mathrm{d}x = -\frac{2m\alpha}{\hbar^2}\psi(0).$$

In our case, then,

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{+\epsilon} - \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{-\epsilon} = -Ak - Ak = -2Bk = -\frac{2m\alpha}{\hbar^2}B.$$

This means we have that

$$k = \frac{m\alpha}{\hbar^2}.$$

From our definition of k, this means that

$$E = -\frac{m\alpha^2}{2\hbar^2}.$$

There is no quantization condition or anything like that, meaning that for our Delta-function potential, we only have one bound state!

- If we move on to scattering states (where $E > 0$), we find that the SE becomes, in the region where $x < 0$:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \quad \rightarrow \quad \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -k^2\psi,$$

where $k \equiv \frac{\sqrt{2mE}}{\hbar}$. This gives the solutions

$$\psi(x) = Ae^{ikx} + Be^{-ikx}.$$

- Similarly, when $x > 0$ we will have

$$\psi(x) = Ce^{ikx} + De^{-ikx}.$$

- Unfortunately, no terms blow up in the limits as $x \to \pm\infty$ due to the i in the exponential; they'll just oscillate to infinity. We can still however impose continuity of ψ at $x = 0$ to get that

$$A + B = C + D.$$

- We can now impose the first-derivative "continuity condition" which, for our weird infinite potential isn't actually a *continuity condition*, but alas:

$$\Delta\left(\frac{\mathrm{d}\psi}{\mathrm{d}x}\right) = \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{0^+} - \left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{0^-} = ik(A - B) - ik(C - D) = ik(C - D - A + D) = -\frac{2m\alpha}{\hbar^2}(A + B).$$

As a note, $\psi(0)$ could also have been $C + D$, it's the same thing. Simplifying this, we get

$$\begin{aligned}
C - D - A + B &= \frac{2m\alpha i}{k\hbar^2}(A + B),\\
C - D &= \frac{2m\alpha i}{k\hbar^2}(A + B) + (A - B),\\
C - D &= A\left(\frac{2m\alpha i}{k\hbar^2} + 1\right) + B\left(\frac{2m\alpha i}{k\hbar^2} - 1\right),\\
C - D &= A(1 + 2i\beta) - B(1 - 2i\beta),
\end{aligned}$$

with $\beta \equiv m\alpha/k\hbar^2$.

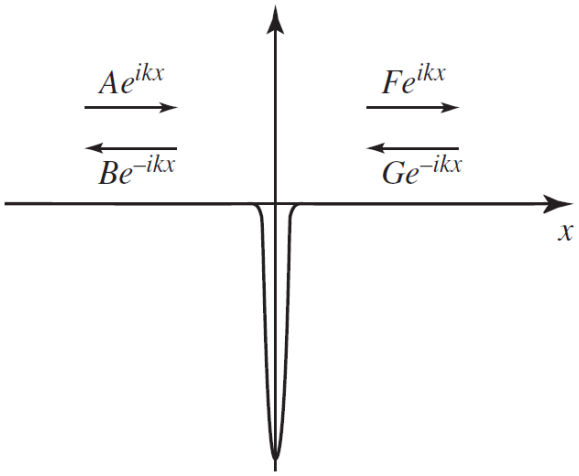

Figure 1: The four wave components of the solutions to the delta function potential.

- Now here we must face the consequences of being unable to apply the limiting boundary conditions: we have two equations to try and narrow down 5 unknowns – A, B, C, D, and k. This clearly won't work, so let's stop to see if we can form a qualitative picture.

- From Fig. 1, we can see that for each region, there is a wave solution propagating left and right.
- In a normal experiment, in which we would be studying something like this, we would be firing particles from only one direction, say, from the left. Since there is no potential after the delta function well, there is now way for anything to come back, so we must have that $G = 0$ (and we will typically know A in advance, too).
- With this, we can now interpret B as the amplitude of the **reflected wave**, and C as the amplitude of the **transmitted wave**. Let's do a little bit of simplification:

$$\begin{cases} C &= A + B, \\ C &= A(1 + 2i\beta) - B(1 - 2i\beta). \end{cases}$$

- We can solve for B in terms of A:

$$\begin{aligned} A + B &= A(1 + 2i\beta) - B(1 - 2i\beta), \\ 0 &= 2A(i\beta) - 2B(1 - i\beta), \\ B(1 - i\beta) &= Ai\beta, \\ B &= \frac{i\beta}{1 - i\beta} A. \end{aligned}$$

  We can now solve for C in terms of A:

$$C = A\left(1 + \frac{i\beta}{1 - i\beta}\right) = \frac{1}{1 - i\beta} A.$$

- We can now examine the ratios of these amplitudes: [1]

$$\boxed{R = \frac{|B|^2}{|A|^2} = \frac{\beta^2}{1 + \beta^2}.} \tag{4.36}$$

[1] As a scattering state, we technically can't examine the probabilities in the same as if we were looking at bound states, since we know that individual stationary scattering states do not themselves form normalizable solutions. But since we are doing ratios here, this is okay.

- R is called the **reflection coefficient**, and it is the probability that the **incident wave** (whose amplitude is A) will reflect back. Similarly, the **transmission coefficent** T is given by

$$\boxed{T = \frac{|C|^2}{|A|^2} = \frac{1}{1+\beta^2},} \tag{4.37}$$

  and it gives the probability that the incident waves transmits through the potential well.

- Additionally, we find that $R + T = 1$, which is as expected.

- Now, since we know that β is as well as what k is, we can write

$$\boxed{R = \frac{1}{1+\frac{2\hbar^2 E}{m\alpha^2}},} \quad \text{and} \quad \boxed{T = \frac{1}{1+\frac{m\alpha^2}{2\hbar^2 E}}.} \tag{4.38}$$

The Finite Square Well

- Let's now revisit the infinite square well, but make it non-infinite. So, what we have now is

$$V(x) = \begin{cases} -V_0 & |x| <= a, \\ 0 & |x| > a. \end{cases} \tag{4.39}$$

- From before, we know that this will permit both bound and scattering states; let's do the bound states first ($E < 0$). First looking at the region $x < a$, we have no potential, so the SE reads

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = E\psi \to \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = k^2\psi,$$

  where $k \equiv \frac{\sqrt{-2mE}}{\hbar}$ since E is negative. This permits the solutions

$$\psi(x) = Ae^{kx} + Be^{-kx}.$$

  But the B term blows up as $x \to -\infty$, so we only have

$$\psi(x) = Ae^{kx} \quad \text{for} \quad x < a. \tag{4.40}$$

- Similarly, for the region $x > a$, we will have similar solutions but the other term will blow up so

$$\psi(x) = Be^{-kx} \quad \text{for} \quad x > a. \tag{4.41}$$

- Inside the well, we have

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} - V_0\psi = E\psi \to \frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\ell^2\psi,$$

  where $\ell \equiv \frac{\sqrt{2m(V_0+E)}}{2m}$. Since $E > -V_0$, then $E + V_0 > 0$ and ℓ is real, as required. This has solutions

$$\psi(x) = C\sin(lx) + D\cos(lx). \tag{4.42}$$

- Before we impose boundary conditions, let's consider the following statement: *If $V(x)$ is an even function, then $\psi(x)$ can always be taken to be either even or odd.* To prove this, we first assume that we have a $\psi(x)$ that satisfies the SE. If we take $x \to -x$, then the SE becomes:

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

  Now obviously the differential $\mathrm{d}(-x)^2 = \mathrm{d}x^2$, and if V is even, then $V(-x) = V(x)$, so we get

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

  We can see that we have retrieved the SE, but with $\psi(-x)$ instead, meaning that $\psi(-x)$ satisfies the SE just as well as $\psi(x)$. Then, since the Hamiltonian operator is a linear operator, then a linear combination of the two ($c_1\psi(x) + c_2\psi(-x)$) will also satisfy the SE.

- This is exactly what we have in this case: $V(x)$ is an even function, and we even have $\psi(x)$ inside the well in the perfect format to motivate taking either the even (cosine) or odd (sine) functions and have either (separately) still satisfy the SE. Let's do the evens part first, meaning we will drop the sine term. Continuity of ψ at $x = a$ requires

$$D\cos(\ell a) = Be^{-kx},$$

and the continuity of $\mathrm{d}\psi/\mathrm{d}x$ requires:

$$-\ell D\sin(\ell a) = -kBe^{-kx}.$$

Dividing two, we get:

$$\ell\tan(\ell a) = k. \tag{4.43}$$

- Now, this does indeed give us the allowed energies, just like we did for previous cases. However, this is terribly hard to parse, so let's massage it a little bit. First, we define

$$z \equiv \ell a, \quad \text{and} \quad z_0 = \frac{a}{\hbar}\sqrt{2mV_0}. \tag{4.44}$$

Then, with a little bit of algebra, we can find

$$\tan z = \sqrt{\left(\frac{z_0}{z}\right)^2 - 1}. \tag{4.45}$$

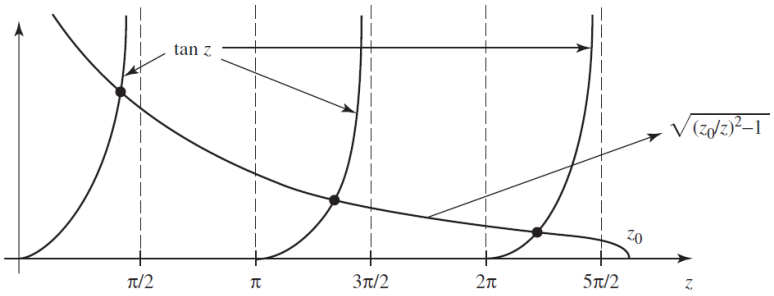

Figure 2: Plots of either side of Eq. (4.45); the line crossing points are allowed values of energy.

- Now, these solutions on their own are not particularly illuminating. But we have two limiting cases that are kinda interesting. The first is when the well gets wide and/or deep; i.e. we increase z_0. This has the graphical effect of pushing the square root curve upwards and making it flatter. We can tell, then, that this would increase the number of solutions, and if we let $z_0 \to \infty$, we end up with an infinite number of solutions. We can also tell that those solutions would correspond to $z = n\pi/2$ for odd n:

$$\frac{n\pi}{2} = z = la = a\frac{\sqrt{2m(E+V_0)}}{\hbar} \to E + V_0 = \frac{n^2\pi^2\hbar^2}{2m(2a)^2}.$$

This is exactly the infinite square well solutions with $a \to 2a$ and shifted by V_0. Well, that makes sense.

- The next case is the opposite we let the well get narrower/shallower. All that is involved with this one is that graphically, there will still be an intersection between the two curves regardless of how small z_0 becomes, meaning that there is always at least one bound state.

- The odd solutions and scattering states aren't very illuminating. We didn't even do the former in class at all, and the latter was rushed because we went slow for the first bit of class. As a result, I'm not typing any of it out. Hopefully formalism is next!

5 Formalism

Linear Algebra

- It'll be helpful for me to define some of the stuff from linear algebra, since I haven't taken it. I know what vectors and matrices and stuff are and transformations, but some of the formalities I do not know, so I'll lay some of it out here. This is all from the Appendix in Griffiths.
- A **vector space** is a set of vectors and scalars that satisfy **closure** under *vector addition* and *scalar multiplication.*
- *Vector addition* encompasses a number of things. First, the sum of two vectors is another vector in the vector space, which we'll call V; so for $|a\rangle, |b\rangle \in V$:

$$|a\rangle + |b\rangle = |c\rangle, \quad |c\rangle \in V.$$

- Next, vector addition is commutative:

$$|a\rangle + |b\rangle = |b\rangle + |a\rangle.$$

- It's also associative:

$$|a\rangle + (|b\rangle + |c\rangle) = (|a\rangle + |b\rangle) + |c\rangle.$$

- There exists a *zero* vector such that when added to any vector $|a\rangle$, it gives $|a\rangle$:

$$|a\rangle + |0\rangle = |a\rangle.$$

- Lastly, every vector has an *inverse* (denoted with a negative) such that

$$|a\rangle + |-a\rangle = |0\rangle.$$

- *Scalar multiplcation* also involves a number of properties. First, it is *distributive* (not that the ket $|a\rangle$ and the scalar a are completely different):

$$a(|a\rangle + |b\rangle) = a|a\rangle + a|b\rangle,$$

  and the same the other way around:

$$(a+b)|a\rangle = a|a\rangle + b|a\rangle.$$

- It is associative:

$$a(b|a\rangle) = (ab)|a\rangle.$$

- This is all just normal vector stuff, but it puts it down on the table formally.

- Next, we define a **linear combination** of vectors to be

$$a|a\rangle + b|b\rangle + c|c\rangle + \ldots$$

  for however many vectors we have. By closure, the resultant vector must also be in the vector space. This vector is said to be **linearly dependent** on the set $|a\rangle, |b\rangle, \ldots$, as it can be expressed as a linear combination of them. If any vector *cannot* be expressed as a linear combination of a set of vectors, it is said to be **linearly independent** of them.

- If every vector in the vector space can be expressed as a linear combination of a set of vectors, then that set of vectors is said to **span** the space. If each vector in the set is linearly independent of the others, then the set is called a **basis**. The number of vectors in a basis set is the **dimension** of the vector space.
  - The unit vectors $\hat{i}, \hat{j}, \hat{k}$ are a basis for $\mathbb{R}^3$, as they are all linearly independent of one another, and any other vector in that space can be represented as a linear combination of them. Plus, there are three, which means that the vector space is 3-dimensional, as expected!
- Then, with respect to a given basis
$$|e_1\rangle, |e_2\rangle, \ldots |e_n\rangle,$$
we can represent a vector like
$$|a\rangle = a_1 |e_1\rangle + a_2 |e_2\rangle + \ldots a_n |e_n\rangle,$$
or more concretely, we represent vectors as a tuple of N components (an "N-tuple"):
$$|a\rangle \to (a_1, a_2, \ldots, a_n).$$
- Now, we call a vector space that has an **inner product** as an **inner product space**. The inner product can be thought of as a generalization to the 3-dimensional dot product, and it is denoted with
$$\langle a|b\rangle.$$
- To keep things general, we consider that case that $|a\rangle, |b\rangle$ have complex components. With this, we define threee properties:
$$\begin{aligned}
&\langle b|a\rangle = \langle a|b\rangle^*, \\
&\langle a|a\rangle \geq 0, \quad \text{and} \quad \langle a|a\rangle = 0 \text{ iff } |a\rangle = 0, \\
&\langle a| (b|b\rangle + c|c\rangle) = b\langle a|b\rangle + c\langle a|c\rangle.
\end{aligned}$$
- Now, since the inner product of a vector with itself is greater than (or equal to) zero, we know that its square root must be real. Therefore, we can define the **norm** of a vector to be
$$||a|| = \sqrt{\langle a|a\rangle}.$$
- A vector is **normalized** if it has a norm of 1. Two vectors are **orthogonal** if their dot product vanishes. If we have a set of vectors that are both orthogonal and normalizes (which we can write compactly as
$$\langle a_i|a_j\rangle = \delta_{ij}$$
), then we say it is an **orthonormal** set. With this, we can retrieve the normal relations for dot products in terms of the components:
$$\langle a|b\rangle = a_1^* b_1 + a_2^* b_2 + \ldots a_n^* b_n.$$
- Then, for an orthonormal basis, we can say
$$a_i = \langle e_i|a\rangle.$$
- Lastly, we note that if two vectors have an inner product with themselves, then the inner product between them must exist. This follows from the **Schwartz inequality**:
$$|\langle a|b\rangle|^2 \leq \langle a|a\rangle \langle b|b\rangle. \tag{5.1}$$

Hilbert Spaces

- Now that we have defined some of this stuff, we can continue back to quantum mechanics (but not before a little bit more specifics related to linear algebra in QM).
- First, we can recognize the connection that have sorta already established my seeing that states that operators act on are analogous to vectors that matrices act on. So, we can turn states into vectors and operators into matrices; hence, linear algebra.
- But what vector space are we considering? Well, first we remember that any wavefunction must be normalizable;
$$\int_{-\infty}^{\infty} |\psi(x)| \, \mathrm{d}x < \infty.$$
This is a well-known property: functions that satisfy this are called **square-integrable**. Now, the set of all functions form a vector space themselves, but if we restrict it to to the subset of functions that are square-integrable, it also forms a vector space, and it is this vector space that we call the **Hilbert Space**. Then: *all wave functions live in Hilbert Space.*
- In this space, which can be infinite dimensional, vectors will have infinite components. So, the inner product can be generalized to an integral:
$$\langle f|g\rangle = \int_a^b f^*(x)g(x) \, \mathrm{d}x.$$
- It can be shown that
$$|\int_a^b f^*(x)g(x) \, \mathrm{d}x| = \sqrt{\int_a^b |f(x)|^2 \, \mathrm{d}x \int_a^b |g(x)|^2 \, \mathrm{d}x},$$
which is just the Schwartz inequality, so this Hilbert space satisfies the condition we laid out previous for the inner product.
- We also have, obviously that $\langle f|g\rangle = \langle g|f\rangle^*$, and the inner product of a w.f. with itself,
$$\langle f|f\rangle = \int_a^b |f(x)|^2 \, \mathrm{d}x$$
can be zero if and only if $f(x) = 0$.
- A set of functions is orthonormal is
$$\langle f_m|f_n\rangle = \delta_{mn},$$
which we found for solutions for the infinite square well, for instance.
- Also, a Hilbert space is **complete**, meaning that we can express any function inside it as a linear combination of other functions in the same Hilbert space:
$$f(x) = \sum_n c_n f_n(x),$$
where the coefficients c_n can be found with Fourier's trick (assuming the set is orthonormal):
$$c_n = \langle f_n|f\rangle \, .$$

Hermitian Observables/Operators

- We know that the expectation value of any observable Q is given by

$$\langle Q \rangle = \int \psi^* \hat{Q} \psi \, \mathrm{d}x = \left\langle \psi \,\middle|\, \hat{Q} \,\middle|\, \psi \right\rangle .$$

- We can also write this in slightly different notation; since the operator $\hat{Q}$ acts on the ket $|\psi\rangle$, we can bring it inside the ket; $|\hat{Q}\psi\rangle$. This will just make it a little easier to write what we want to write in a minute.

- Now, if this is an observable, meaning that it represents a quantity that we can physically observe (like energy, position, momentum), then it's expectation value must be real, meaning that

$$\left\langle \psi \,\middle|\, \hat{Q} \,\middle|\, \psi \right\rangle = \left\langle \psi \,\middle|\, \hat{Q} \,\middle|\, \psi \right\rangle^* = \left\langle \hat{Q}\psi \,\middle|\, \psi \right\rangle ,$$

  where we have that $\hat{Q} = \hat{Q}*$ in order for this to be satisfied.

- If we are working with matrices, then we must also transpose. The complex-conjugate and transpose is called the **Hermition conjugate**, and it is denoted with a dagger.

- Let's examine the momentum operator as an example:

$$\langle f \,|\, \hat{p} g \rangle = \int f^* (-i\hbar) \frac{\mathrm{d}g}{\mathrm{d}x} \, \mathrm{d}x = -i\hbar f^* g \Big|_{\infty}^{\infty} + \int_{-\infty}^{\infty} \left(-i\hbar \frac{\mathrm{d}f}{\mathrm{d}x} \right)^* g \, \mathrm{d}x = \langle \hat{p} f \,|\, g \rangle .$$

  Evidently, the momentum operator is Hermitian! It also shows that the derivative part in there makes it not just a simple complex conjugate, because in that case, obviously it wouldn't be Hermitian. That is why we, in general, use the dagger notation regardless if it is a pure scalar, contains derivatives, or is a matrix.

- Let's find what the Hermitian conjugate of the operator $\hat{Q} = \dfrac{\mathrm{d}}{\mathrm{d}x}$:

$$\left\langle f \,\middle|\, \hat{Q} g \right\rangle = \int f^* \frac{\mathrm{d}g}{\mathrm{d}x} \, \mathrm{d}x = f^* g \Big|_{\infty}^{\infty} + \int_{-\infty}^{\infty} \left(-\frac{\mathrm{d}f}{\mathrm{d}x} \right)^* g \, \mathrm{d}x.$$

  Thus,

$$\left(\frac{\mathrm{d}}{\mathrm{d}x} \right)^\dagger = -\frac{\mathrm{d}}{\mathrm{d}x}.$$

Determinate States

- Determinate states of a particular operator that represents an observable are those that have no variance; every measurement of that particular observable will give back the same value. So,

$$\sigma_Q = \left\langle (Q - \langle Q \rangle)^2 \right\rangle = \left\langle \left(\hat{Q} - q \right)^2 \right\rangle = \left\langle \psi \,\middle|\, \left(\hat{Q} - q \right)^2 \,\middle|\, \psi \right\rangle .$$

- As an observable, $\hat{Q}$ is Hermitian, and so is $\hat{Q} - q$ (this can be easily shown), meaning we can bring one of them over to the bra:

$$= \left\langle \left(\hat{Q} - q \right)^2 \psi \,\middle|\, \left(\hat{Q} - q \right)^2 \psi \right\rangle = 0.$$

  Now we have the inner product of a vector in Hilbert space with itself, and we know from before that the only way that this can be true is if the vector itself is zero:

$$\left| \left(\hat{Q} - q \right) \psi \right\rangle = 0 \quad \rightarrow \quad \hat{Q} \,|\psi\rangle = q \,|\psi\rangle .$$

- This is just an eigenvalue equation, which means that *a determinate state of an operator $\hat{Q}$ is an eigenfunction of that operator.*
- The TISE is an eigenvalue equation, which means that solutions to it (that are normalizable!! looking at you free particle solutions...) are determinate states of the Hamiltonian, or energy.
- Next: Eigenvalues of a Hermitian operator are real.
- Proof: If $\hat{Q}$ is Hermitian and has eigenvalue q

$$\langle \hat{Q}f|f\rangle = \langle f|\hat{Q}f\rangle \Rightarrow q^* \langle f|f\rangle = q \langle f|f\rangle .$$

  Now the eigenfunction f cannot be zero, because zero-eigenfunctions are not actual eigenfunctions. If they were, then it would have every eigenvalue for every observable, which obviously shouldn't be the case. Thus, its inner product with itself cannot be zero, and it must be that $q^* = q$ for every eigenfunction f.
- Next: Eigenfunctions of a Hermitian operator with distinct eigenvalues are orthogonal.
- Proof: Consider two eigenfunctions f and g of operator $\hat{Q}$: $\hat{Q}f = qf$ and $\hat{Q}g = q'g$. Since $\hat{Q}$ is Hermitian,

$$\left\langle \hat{Q}f \,\middle|\, g \right\rangle = \left\langle f \,\middle|\, \hat{Q}g \right\rangle \rightarrow q^* \langle f|g\rangle = q' \langle f|g\rangle .$$

  We just proved $q^* = q$, so

$$q \langle f|g\rangle = q' \langle f|g\rangle .$$

  Again, neither f nor g can be zero themselves, and since they live in Hilbert space, their inner product exists. Since $q \neq q'$, then it must be that $\langle f|g\rangle = 0$.
- Lastly: Eigenfunctions of a Hermitian operator are **complete**.
- There is no proof for this one. We can show that it is the case for a few examples, like for the infinite square well due to Dirichlet's theorem, but in general we can't really show this. In fact, we will take this as an axiom in our theory. Well, really, we take is as a restriction on the eigenfunctions and operators that we look at, but it's the same thing.

- Now, what if we have a continuous spectra? We have just been considering discrete spectra (where spectra is the eigenvalues). In this case, we know from the free particle that the eigenfunctions are not normalizable for any momentum.
- Let's examine this a little bit more: the eigenfunctions of the momentum operator are simple plane waves as we found out before:

$$f_p(x) = Ae^{ipx/\hbar}.$$

- Which, as we just stated, we obviously cannot normalize. But, we can we find anything? Let's just try and test the orthogonality condition and see what happens:

$$\langle f_{p'}|f_p\rangle = \int_{-\infty}^{\infty} f_{p'}(x) f_p(x)\, \mathrm{d}x = |A|^2 \int_{-\infty}^{\infty} e^{-i(p'-p)x/\hbar}\, \mathrm{d}x.$$

  This is a common identity, it gives is a delta function:

$$\langle f_{p'}|f_p\rangle = |A|^2 2\pi\hbar\delta(p'-p).$$

- If we let $A = 1/\sqrt{2\pi\hbar}$, then the momentum eigenfunctions become

$$f_p(x) = \frac{1}{\sqrt{2\pi\hbar}} e^{ipx/\hbar},$$

and the "orthogonality" condition becomes

$$\langle f_{p'} | f_p \rangle = \delta(p' - p).$$

- This pseudo-orthogonality is called **Dirac orthogonality**. It'll still blow up if $p' = p$ (this is just the normalization, of course), but for any $p' \neq p$, it is zero reflecting orthogonality.
- On top of this, these are still complete, as we found. For a continuous spectra, it turns from a sum to an integral:

- Going back to the discrete case, we know that if we have a complete orthonormal set $\{|f_n\rangle\}$, we can say

$$\langle f | = \sum_i c_i \langle f_i | .$$

- Then should we want to determine the nth coefficient, all we do is

$$\langle f_n | f \rangle = \sum_i c_i \langle f_n | f_i \rangle = \sum_i c_i \delta_{in} = c_n.$$

Generalized Statistical Interpretation and the Uncertainty Principle

- What we have done is great, but let's ground it a little bit into what we are doing in QM. The first interpretation that we make is that for an observable $\hat{Q}$ with discrete spectrum, the probability of measuring Q and getting an eigenvalue q_n associated with the eigenfunction $f_n(x)$ is $|c_n|^2$, which is the corresponding Fourier coefficient that we just found.
- There are a number of other related and relatively intuitive results that we could keep quoting and deriving, but they are things that we have already alluded to before, and would just be rephrasing in a more abstract light.
- However, we will look at the generalized version of the uncertianty principle, as we just quoted it in the previous chapter without any sort of derivation.
- First, we know from before that for some observable A:

$$\sigma_A^2 = \left\langle \left(\hat{A} - \hat{A}\right)\psi \,\middle|\, \left(\hat{A} - \hat{A}\right)\psi \right\rangle = \langle f | f \rangle ,$$

where $|f\rangle = \left(\hat{A} - \hat{A}\right)\psi$. Similarly, for some other observable B

$$\sigma_B^2 = \left\langle \left(\hat{B} - \hat{B}\right)\psi \,\middle|\, \left(\hat{B} - \hat{B}\right)\psi \right\rangle = \langle g | g \rangle ,$$

where $|g\rangle = \left(\hat{B} - \hat{B}\right)\psi$. The product of the variances is

$$\sigma_A^2 \sigma_B^2 = \langle f | f \rangle \langle g | g \rangle \geq |\langle f | g \rangle|^2,$$

which follows from the Schwartz inequality.

- Now, in general $\langle f|g\rangle$ may be complex, let's call it z for a moment. We know that

$$|z|^2 = \mathrm{Re}[z]^2 + \mathrm{Im}[z]^2 \geq \mathrm{Im}[z]^2,$$

since $\Re[z]^2 \geq 0$, as it's real. We can rewrite the imaginary part in terms of z itself:

$$|z|^2 \geq \left[\frac{1}{2i}\left(z - z^*\right)\right]^2.$$

- Plugging back in our $\langle f|g\rangle$:

$$\sigma_A^2\sigma_B^2 \geq \left[\frac{1}{2i}\left(\langle f|g\rangle - \langle g|f\rangle\right)\right]^2.$$

We can write

$$\begin{aligned}\langle f|g\rangle &= \left\langle \psi \,\middle|\, \left(\hat{A} - \langle A\rangle\right)\left(\hat{B} - \langle B\rangle\right) \,\middle|\, \psi \right\rangle, \\ &= \left\langle \psi \,\middle|\, \hat{A}\hat{B} - \hat{A}\langle B\rangle - \langle A\rangle \hat{B} + \langle A\rangle\langle B\rangle \,\middle|\, \psi \right\rangle.\end{aligned}$$

Note that $\langle A\rangle$ and $\langle B\rangle$ are just numbers, so we can move them around however we like:

$$\begin{aligned}&= \left\langle \psi \,\middle|\, \hat{A}\hat{B} \,\middle|\, \psi \right\rangle - \langle B\rangle \left\langle \psi \,\middle|\, \hat{A} \,\middle|\, \psi \right\rangle - \langle A\rangle \left\langle \psi \,\middle|\, \hat{B} \,\middle|\, \psi \right\rangle + \langle A\rangle\langle B\rangle\langle \psi \,|\, \psi\rangle, \\ &= \left\langle \hat{A}\hat{B} \right\rangle - \langle B\rangle\langle A\rangle - \langle A\rangle\langle B\rangle + \langle A\rangle\langle B\rangle, \\ \langle f|g\rangle &= \langle \hat{A}\hat{B}\rangle + \langle A\rangle\langle B\rangle.\end{aligned}$$

- Similarly, we find that

$$\langle g|f\rangle = \langle \hat{B}\hat{A}\rangle + \langle A\rangle\langle B\rangle,$$

so

$$\langle f|g\rangle - \langle g|f\rangle = \langle \hat{A}\hat{B}\rangle - \langle \hat{B}\hat{A}\rangle = \langle [\hat{A}, \hat{B}]\rangle.$$

With this,

$$\boxed{\sigma_A^2\sigma_B^2 \geq \left(\frac{1}{2i}\langle [\hat{A}, \hat{B}]\rangle\right)^2.}$$

- Let's test this with $\hat{x}$ and $\hat{p}$. We know their commutator is $i\hbar$:

$$\sigma_x^2\sigma_p^2 \geq \left(\frac{1}{2i}i\hbar\right)^2 = \left(\frac{\hbar}{2}\right)^2.$$

But since the standard deviations are positive by definition,

$$\boxed{\sigma_x\sigma_p \geq \frac{\hbar}{2}.} \tag{5.2}$$

- Nice!

- What this basically says is that for any pair of non-commuting observables, there will be inherent uncertainty with simultaneous measurements of them. In fact, there is no way at all for simultanous measurements to be made, which means that we cannot construct states that are eigenstates of both operators. When we turn to the hydrogen atom, we will find that the z-component of spin and the magnitude squared of angular momentum commute, which means that we can form states that are eigenstates of both; in fact, that is how we will label generic states. We will see this when we get there.

- For one more thing, let's consider the Hamiltonian operator and some other generic observable Q. This requires a bit more work, but it's not terribly important. Regardless, it can be shown that

$$\sigma_H^2 \sigma_Q^2 \geq \left(\frac{1}{2i} \langle [\hat{H}, \hat{Q}] \rangle \right)^2 = \left(\frac{1}{2i} \frac{\hbar}{i} \frac{\mathrm{d} \langle Q \rangle}{\mathrm{d}t} \right)^2 = \left(\frac{\hbar}{2} \right)^2 \left(\frac{\mathrm{d} \langle Q \rangle}{\mathrm{d}t} \right)^2.$$

  Doing some rearranging:

$$\sigma_H \frac{\sigma_Q}{\mathrm{d} \langle Q \rangle / \mathrm{d}t} \geq \frac{\hbar}{2}.$$

- Now, we can make a few definitions, the first is which is quite obvious: $\Delta E \equiv \sigma_H$. Next, we can interpret the second term on the left as the amount of time it takes for the expectation value of Q to change by 1 standard deviation. As such, we can define this as Δt, so that we get

$$\boxed{\Delta E \Delta t \geq \frac{\hbar}{2}.} \tag{5.3}$$

- This is the energy-time uncertainty principle, and it is a little bit misleading. This is not just the "change in energy" and the "change in time", it has to do with uncertainties. Further, the "change in time" is not just a generic time; it is related only to one particle observable, and means something entirely differnet for another observable.

- The basic interpretation is that how quickly an observable's expectation value changes is inversely proportional to the uncertainty in the energy. Roughly speaking, the faster an variable changes, the less we know about the energy.o

6 Three Dimensional Schrodinger Equation

- Going to three dimensions is relatively straightforward:

$$i\hbar \frac{\partial \psi}{\partial t} = -\frac{\hbar^2}{2m} \boldsymbol{\nabla}^2 \psi + V\psi. \tag{6.1}$$

- Now we have that the probability of finding a particle in an infinitesimal *volume* $\mathrm{d}^3\mathbf{r}$ is given by $|\psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3\mathbf{r}$, and the normalization condition is now

$$\int |\psi(\mathbf{r}, t)|^2 \, \mathrm{d}^3\mathbf{r} = 1. \tag{6.2}$$

- Our first set of assumptions/simplifications that we will make in this regime is that our potential is only dependent on the distance $r = |\mathbf{r}|$ as well as not dependent on time; this is called a *central potential*, and it motivates the switching of coordinate systems from cartesian to spherical. With this, the **Laplacian** $\boldsymbol{\nabla}^2$ becomes

$$\boldsymbol{\nabla}^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \left(\frac{\partial^2}{\partial \phi^2} \right). \tag{6.3}$$

- With our assumption of a time-independent potential, the TISE now reads

$$-\frac{\hbar^2}{2m} \left[\frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial \psi}{\partial r} \right) + \frac{1}{r^2 \sin\theta} \frac{\partial}{\partial \theta} \left(\sin\theta \frac{\partial \psi}{\partial \theta} \right) + \frac{1}{r^2 \sin^2\theta} \left(\frac{\partial^2 \psi}{\partial \phi^2} \right) \right] + V\psi = E\psi.$$

- There is more annoying simplifications to be made, which I will not do. We will now use separation of variables and split the wave function into the radial and angular parts:

$$\psi(r, \theta, \phi) = R(r) Y(\theta, \phi). \tag{6.4}$$

Our choice of separation constant as $\ell(\ell+1)$ lets later results make more sense and makes things easier to solve. This comes at the cost of making literally zero sense at the moment, but that's kinda how things are done in QM - we just follow ad hoc solutions that people many decades ago came up with. With this, we get two equations:

$$\begin{cases} \dfrac{1}{R}\dfrac{\mathrm{d}}{\mathrm{d}r}\left(r^2\dfrac{\mathrm{d}R}{\mathrm{d}r}\right) - \dfrac{2mr^2}{\hbar^2}[V(r)-E] = \ell(\ell+1), \\ \dfrac{1}{Y}\left[\dfrac{1}{\sin\theta}\dfrac{\partial}{\partial\theta}\left(\sin\theta\dfrac{\partial\psi}{\partial\theta}\right) + \dfrac{1}{\sin^2\theta}\left(\dfrac{\mathrm{d}^2\psi}{\mathrm{d}\phi^2}\right)\right]. \end{cases} \tag{6.5}$$

- Let's look at angular equation first. We can apply separation of variables again to have

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi), \tag{6.6}$$

and if we choose our separation constant to be m^2, we get another set of two equations:

$$\begin{cases} \dfrac{1}{\Theta}\left[\sin\theta\dfrac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\dfrac{\mathrm{d}\Theta}{\mathrm{d}\theta}\right)\right] + \ell(\ell+1)\sin^2\theta = m^2, \\ \dfrac{1}{\Phi}\dfrac{\mathrm{d}^2\Phi}{\mathrm{d}\phi^2} = -m^2. \end{cases} \tag{6.7}$$

- The ϕ equation is super easy to solve:

$$\Phi(\phi) = Ae^{im\phi} + Be^{-im\phi}. \tag{6.8}$$

What we will do here is let m run negative so that A and B become related, then move it into the θ equation so all we have is

$$\Phi(\phi) = e^{im\phi}. \tag{6.9}$$

- As an azimuthal angle, we expect that $\Phi(0) = \Phi(2\pi)$ since $0 = 2\pi$. This means that we must have

$$e^{im2\pi} = 1 \quad \rightarrow \quad m = 0, \pm1, \pm2, \ldots;$$

m must be an integer!

- Moving to the polar equation, it turns out that if we do some rearranging and some comparing, we find that the solutions are exactly the **associated Legendre functions** (with a constant):

$$\Theta(\theta) = AP_\ell^m(\cos\theta), \tag{6.10}$$

where $P_\ell^m(\cos\theta)$ is associated Legendre function defined by

$$P_\ell^m(x) \equiv (-1)^m(1-x^2)^{m/2}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^m P_\ell(x), \tag{6.11}$$

and $P_\ell(x)$ is the ℓth **associated Legendre polynomial**, and it is given by the **Rodrigues formula**:

$$P_\ell(x) = \frac{1}{2^\ell \ell!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^\ell (x^2-1)^\ell. \tag{6.12}$$

- This is why we chose the separation constant to be that funky form. I suppose we could have just let it be whatever, then once we did the rearranging a bit later, we could recognize that it is almost identical to the Legendre differential equation, after which we could make the substitution. Either way, for these notes, I wouldn't have written it down so it doesn't really matter. By the way, we defined m to be able to run negative, and as it stands, negative m's make no sense. It turns out that we define the associated Legendre functions with negative m like so:

$$P_\ell^{-m}(x) = (-1)^m\frac{(\ell-m)!}{(\ell+m)!}P_\ell^m(x). \tag{6.13}$$

- Now, for the Rodrigues formula to make any sense at all, we must have that ℓ be a non-negative integer (there is no definition for a negative ℓ). Further, m cannot exceed l, else we get zero.[2]

- With this, then, we must have that for any given value of ℓ, there are $2\ell+1$ valid values of m that are both possible and non-zero - it's the range from $-\ell$ to ℓ. These quantization conditions will come in handy in a little while when we more closely examine angular momentum.

- The last thing that we can do for the angular equation is normalize it. We can choose our normalization constants such that we can normalize the radial and angular part separately:

$$\int |\psi|^2 \, \mathrm{d}^3\mathbf{r} = \int |\psi|^2 r^2 \sin\theta \, \mathrm{d}r\mathrm{d}\theta\mathrm{d}\phi = \int_0^\infty |R|^2 r^2 \, \mathrm{d}r \int_0^{2\pi} \int_0^\pi |Y|^2 \sin\theta \, \mathrm{d}\theta\mathrm{d}\phi.$$

- This normalization is quite complex. It turns out that it is

$$\boxed{Y_\ell^m = \sqrt{\frac{(2\ell+1)}{4\pi}\frac{(\ell-m)!}{(\ell+m)!}} e^{im\phi} P_\ell^m(\cos\theta).} \tag{6.14}$$

- These are called **spherical harmonics**.

- Moving now to the radial equation:

$$\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2 \frac{\mathrm{d}R}{\mathrm{d}r}\right) - \frac{2mr^2}{\hbar^2}[V(r) - E]R = \ell(\ell+1)R. \tag{6.15}$$

- If we define $u(r) \equiv rR(r)$, then this becomes

$$-\frac{\hbar^2}{2m} + \left(V + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right) u = Eu. \tag{6.16}$$

- This is identical in form to the TISE, with the extra potential term which we call the **effective potential**. It turns out that this has a "centrifugal" effect.

- Unfortunately this is as far as we can go in the general because we need to know the form of the potential before doing anything else.

The Hydrogen Atom

- One such potential is that of an electron orbiting a "stationary" positively charged particle - a.k.a. the hydrogen atom. This potential is

$$V(r) = -\frac{e^2}{4\pi\epsilon_0}\frac{1}{r}, \tag{6.17}$$

  and with it the radial equation becomes

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2u}{\mathrm{d}r^2} + \left(-\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \frac{\hbar^2}{2m}\frac{\ell(\ell+1)}{r^2}\right) u = Eu. \tag{6.18}$$

- We are interested in bound states here, because a scattering state isn't the hydrogen atom. First, we can tidy up the notation. If we let $k \equiv \sqrt{-2mE}/\hbar$, $\rho = kr$ and $\rho_0 = me^2/2\pi\epsilon_0\hbar^2 k$, then we get

$$\frac{\mathrm{d}^2u}{\mathrm{d}\rho^2} = \left(1 - \frac{\rho_0}{\rho} + \frac{\ell(\ell+1)}{\rho^2}\right) u. \tag{6.19}$$

[2] This is because $P_\ell(x)$ is by definition an ℓth order polynomial. If m were to be greater than ℓ, then in the definition of the associated Legendre functions we would be differentiating an ℓth order polynomial more than ℓ times, which is zero.

- We consider the solutions in the extremes. When $\rho \to \infty$, the 2nd and 3rd term vanish so all we have is

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = u, \tag{6.20}$$

which has the general solution

$$u(\rho) = Ae^{-\rho} + Be^{\rho}. \tag{6.21}$$

- But in this limit, the B term blows up, so all we have is

$$u(\rho) = Ae^{-\rho}. \tag{6.22}$$

- Next, when $\rho \to 0$, the first and second terms vanish and only the third contributes so

$$\frac{\mathrm{d}^2 u}{\mathrm{d}\rho^2} = \frac{\ell(\ell+1)}{\rho^2} u, \tag{6.23}$$

which has general solution

$$u(\rho) = C\rho^{\ell+1} + D\rho^{-\ell}. \tag{6.24}$$

- The D term blows up in this limit, so

$$u(\rho) = C\rho^{\ell+1}. \tag{6.25}$$

- What we do next is "peel off" this asymptotic behavior by attempting to find a function $v(\rho)$ such that

$$u(\rho) = \rho^{\ell+1} e^{-\rho} v(\rho). \tag{6.26}$$

- The radial equation in terms of this $v(\rho)$ is

$$\rho \frac{\mathrm{d}^2 v}{\mathrm{d}\rho^2} + 2(\ell + 1 - \rho)\frac{\mathrm{d}v}{\mathrm{d}\rho} + [\rho_0 - 2(\ell+1)]\, v = 0. \tag{6.27}$$

- The last big assumption we make is that we can express this function $v(\rho)$ as a power series in ρ:

$$v(\rho) = \sum_{j=0}^{\infty} c_j \rho^j. \tag{6.28}$$

- With this, the radial equation becomes

$$\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j + 2(\ell+1)\sum_{j=0}^{\infty} j(j+1)c_{j+1}\rho^j - 2\sum_{j=0}^{\infty} j c_j \rho^j + [\rho_0 - 2(\ell+1)]\sum_{j=0}^{\infty} c_j \rho_j = 0, \tag{6.29}$$

and if we equate like-power coefficients, we get

$$j(j+1)c_{j+1} + 2(\ell+1)(j+1)c_{j+1} - 2jc_j + [\rho_0 - 2(\ell+1)]c_j = 0. \tag{6.30}$$

- We can turn this into a recursion relation:

$$c_{j+1} = \left(\frac{2(j+\ell+1) - \rho_0}{(j+1)(j+2\ell+2)}\right) c_j. \tag{6.31}$$

- It turns out however, that after doing all this and plugging back into our equation for $u(\rho)$, it still diverges in one of the limits, which is exactly what we didn't want. The only way to fix this with our current assumptions is for the series to terminate eventually at some N such that $C_{N-1} \neq 0$ and $C_N = 0$, after which all the rest of the coefficients will be zero by virtue of the recursion relation.

- Using the recursion relation and the assumption that the series must terminate, we end up getting something like
$$2(N+\ell)-\rho_0=0. \tag{6.32}$$
Defining $n\equiv N+\ell$, we get
$$\rho_0=2n. \tag{6.33}$$

- But ρ_0 determines the energy; with this, we get that
$$E=-\frac{me^4}{8\pi^2\epsilon_0^2\hbar^2\rho_0^2}, \tag{6.34}$$
meaning the allowed energies are
$$E_n=-\left[\frac{m}{2\hbar^2}\left(\frac{e^2}{4\pi\epsilon_0}\right)^2\right]\frac{1}{n^2}=\frac{E_1}{n^2}, \tag{6.35}$$
where $E_1=-13.6\,\text{eV}$. This is the **Bohr Formula**.

- Now it turns out that the $N-1$th order polynominals whose coefficients are determined by the above recursion relation are the **associated Laguerre polynomials** given by
$$L_q^p(x)=(-1)^p\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^p L_{p+q}(x), \tag{6.36}$$
where $L_q(x)$ is the qth **Laguerre polynomial** defined by
$$L_q(x)=\frac{e^x}{q!}\left(\frac{\mathrm{d}}{\mathrm{d}x}\right)^q(e^{-x}x^q). \tag{6.37}$$

- $v(\rho)$ can then be written as
$$R_{n\ell}(r)=\frac{1}{r}\rho^{\ell+1}e^{-\rho}L_{n-\ell-1}^{2\ell+1}(2\rho), \tag{6.38}$$
and our final normalized wave function for the hydrogen atom is
$$\boxed{\psi_{n\ell m}=\sqrt{\left(\frac{2}{na}\right)^3\frac{(n-\ell-1)!}{2n(n+\ell)!}}e^{-r/na}\left(\frac{2r}{na}\right)^\ell\left[L_{n-\ell-1}^{2\ell+1}(2r/na)\right]Y_\ell^m(\theta,\phi).} \tag{6.39}$$

- Note that this is dependent on *three* quantum numbers. n characterizes the energy, as we found, and for a given value of n, there are n values of ℓ (from the equation we got from the condition for the power series terminating), and there are $2\ell+1$ values of m for each value of ℓ. These second two quantum numbers are related to the angular momentum, as we will find.

Angular Momentum

- If two operators $\hat{A}$ and $\hat{B}$ commute, then we can construct a function that is simultaneously an eigenfunction of both operators. This comes from the fact that the generalized uncertainty principle gives no minimum uncertainty for simultaneous measurements of both operators. It follows, then, that we can know both quantities at any given time with perfect precision, meaning that we can define a state by both quantities.

- We know that the position operator (in some direction) does *not* commute with the momentum operator (in the same dimension), meaning that we cannot construct a state that is a simultaneously an eigenfunction of both position and momentum (in the same direction).

- What about *angular* momentum?

- As a recap, angular momentum is defined (classically) by

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = (yp_z - zp_y)\hat{i} + \dots. \tag{6.40}$$

- Now, $L_x = yp_z - zp_y$ as we just saw. In operator form,

$$\hat{L}_x = \hat{y}\hat{p}_z - \hat{z}\hat{p}_y = \frac{1}{i\hbar}[\hat{L}_y, \hat{L}_z]. \tag{6.41}$$

- So,

$$[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x. \tag{6.42}$$

- It turns out that in general this is *cyclic*:

$$[\hat{L}_a, \hat{L}_b] = i\hbar\epsilon^{abc}\hat{L}_c, \tag{6.43}$$

  where ϵ^{abc} is the **Levi-Civita** symbol.

- It would seem, then, that we cannot construct states that are simultaneously eigenfunctions of any two components of angular momentum, unlike ordinary momentum.

- However, we can examine the *magnitude* of the angular momentum

$$\mathbf{L}^2 = L_x^2 + L_y^2 + L_z^2. \tag{6.44}$$

- Then, (dropping the hats for simplicity as well as the bolding of the magnitude)

$$[\mathbf{L}^2, L_z] = [L_x^2, L_z] + [L_y^2, L_z] + [L_z^2, L_z]. \tag{6.45}$$

- Obviously the last term commutes. The first term is

$$\begin{aligned}
[L_x^2, L_z] &= L_xL_xL_z - L_zL_xL_x && (6.46)\\
&= L_xL_xL_z - L_xL_zL_x + L_xL_zL_x - L_zL_xL_x && (6.47)\\
&= L_x[L_x, L_z] + [L_x, L_z]L_z && (6.48)\\
&= -i\hbar(L_xL_y + L_yL_x) && (6.49)\\
&= -i\hbar\{L_x, L_y\}, \to [L_y^2, L_z] \qquad = i\hbar L_x, L_y, && (6.50)
\end{aligned}$$

  where the final step follows from the cyclic nature of the angular momentum operators (doing the second commutator has an identical process). Then, if the last term is zero and the others cancel,

$$\to [L^2, L_z] = 0 \tag{6.51}$$

- This means that while we cannot know more than one component of the angular momentum at a time, we can however one component (we typically choose the z component) and the *total* angular momentum.

- It also follows that are able to contruct a function f such that

$$L^2 f = \lambda f \quad \text{and} \quad L_z f = \mu f. \tag{6.52}$$

- Let's construct now two new operators $L_\pm = L_x \pm iL_y$. It follows pretty simply that

$$[L_z, L_\pm] - \pm\hbar L_\pm, \quad \text{and} \quad [L^2, L_\pm] = 0. \tag{6.53}$$

- In a similar vein as with the ladder operators we found for the harmonic oscillator, we make the claim that if f is an eigenstate of L^2 and L_z, then so too is $L_\pm f$ with eigenvalues we will find now.
- First,
$$L^2(L_\pm f) = L_\pm(L^2 f) = \lambda(L_\pm)f, \tag{6.54}$$
which is trivial since $L_\pm$ commutes with L^2. We see that is has the same eigenvalue, as well.
- For L_z:
$$\begin{aligned} L_z(L_\pm f) &= [L_z, L_\pm]f + L_\pm(L_z f) && (6.55)\\ &= \pm\hbar L_\pm f + \mu L_\pm f && (6.56)\\ &= (\mu \pm \hbar)L_\pm f. && (6.57)\end{aligned}$$
- It turns out that the analogy with the ladder operators is quite a good analogy! Acting with the ladder operator on a state that is an eigenfunction of L_z increases/decreases its eigenvalue by $\pm\hbar$.
- But there are a few restrictions to this. First, it should be obvious that a single component of the angular momentum cannot go above the total magnitude, meaning that μ cannot go above λ. Then, there must exist some maximum rung of our ladder (more pedantically, there must exist some top *eigenfunction* f_t) such that $L_+ f_t = 0$. The top rung, then, has eigenvalue $L_z f_t = \hbar\ell f_t$ where ℓ is some integer. This functions L^2 eigenvalue is still λ.
- Now,
$$\begin{aligned} L_\pm L_\mp &= (L_x \pm iL_y)(L_x \mp iL_y) = L_x^2 + L_y^2 \mp i(L_x L_y - L_y L_x) && (6.58)\\ &= L^2 - L_z^2 \pm \hbar L_z, && (6.59)\end{aligned}$$
or, with L^2 on one side this reads
$$L^2 = L_\pm L_\mp + L_z^2 \mp \hbar L_z. \tag{6.60}$$
- Then,
$$L^2 f_t = \lambda f_t = (L_- L_+ + L_z^2 + \hbar L_z)f_t = (0 + \hbar^2\ell^2 + \hbar^2\ell)f_t = \hbar^2\ell(\ell+1)f_t. \tag{6.61}$$
Hence,
$$\lambda = \hbar^2\ell(\ell+1). \tag{6.62}$$
- The exact same logic applies to sending the eigenvalue of L_z in the other direction - there is some *bottom* rung (eigenfunction) f_b that has $L_z f_b = \hbar\bar{\ell} f_t$, and we similarly find
$$\lambda = \hbar^2\bar{\ell}(\bar{\ell}+1). \tag{6.63}$$
- These must be equal, of course, and for this to be the case there are two possibilities: $\bar{\ell} = \ell + 1$ or $\bar{\ell} = -\ell$. The former is ridiculous since the bottom rung cannot be *above* the top, so it must be that the latter is true.
- Therefore, the eigenvalues of L_z are integer multiples of $\hbar$, call this integer m, where m is restricted to move between $-\ell$ and ℓ for some value of ℓ (seem familiar yet?).
- More completely:
$$L^2 f_\ell^m = \hbar^2\ell(\ell+1)f_\ell^m \quad \text{and} \quad L_z f_\ell^m = \hbar m f_\ell^m. \tag{6.64}$$
- Interestingly, we never restricted ℓ to have purely integer values, we simply let it correspond the to multiple of $\hbar$ that was the eigenvalue of the top rung. The only restriction we now have is that there are an integer number of steps between $-\ell$ and ℓ, meaning that ℓ can actually be a *half-integer*.

- But what are these eigen-functions f_ℓ^m? Well, we know that the equation for angular momentum is $\mathbf{L} = \mathbf{r} \times \mathbf{p}$, or with the quantum prescription for momentum we get

$$\mathbf{L} = -i\hbar(\mathbf{r} \times \boldsymbol{\nabla}). \tag{6.65}$$

- The gradient, in spherical coordinates is

$$\boldsymbol{\nabla} = \frac{\partial}{\partial r}\,\hat{r} + \frac{1}{r}\frac{\partial}{\partial \theta}\,\hat{\theta} + \frac{1}{r\sin\theta}\frac{\partial}{\partial \phi}\,\hat{\phi}. \tag{6.66}$$

- Therefore, with $\mathbf{r} = r\,\hat{r}$, doing the cross product we find that

$$\mathbf{L} = -i\hbar\left(\frac{\partial}{\partial \theta}\,\hat{\phi} - \frac{1}{\sin\theta}\frac{\partial}{\partial \phi}\,\hat{\theta}\right). \tag{6.67}$$

- With this, then,

$$L_z = -i\hbar\frac{\partial}{\partial \phi}. \tag{6.68}$$

- We can now assemble the eigenvalue equation for this operator:

$$\hat{L}_z f_\ell^m = -i\hbar\frac{\mathrm{d}}{\mathrm{d}\phi} f_\ell^m = \hbar m f_\ell^m. \tag{6.69}$$

- This is exactly the azimuthal equation we solved for in the beginning!

- Next, after some algebra (technically calculus, I guess) we find

$$\mathbf{L}^2 = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right], \tag{6.70}$$

  so our eigenvalue equation is

$$\hat{L}^2 f_\ell^m = -\hbar^2\left[\frac{1}{\sin\theta}\frac{\mathrm{d}}{\mathrm{d}\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] f_\ell^m = \hbar^2\ell(\ell+1) f_\ell^m. \tag{6.71}$$

  This is the angular equation that we solved for!

- Thus, we have found that the eigenfunctions of both operators are the spherical harmonics. The full normalized wave function is therefore an eigenfunction of $\hat{L}_z$, $\hat{L}^2$, and H, meaning all of those operators commute.

- Another interesting bit: going this route, we have found that ℓ (and therefore m) can actually take *half*-integer values. The only discretization condition we found is that m must go from $-\ell$ to ℓ in integer steps. This by no means implies that ℓ must be an integer, since we can very well go from $-1/2$ to $1/2$ in one integer step. This missing piece is spin.

Spin

- All particles have both orbital angular momentum, given by $\mathbf{L}$ that we looked at just now, and *spin* angular momentum given by $\mathbf{S}$. Actually, the theory follows exactly the same since it's derived from the same fundamental rotational symmetry any system must have:

$$[S_i, S_j] = i\hbar\epsilon^{ijk}S_k. \tag{6.72}$$

- As we will see, however, eigenstates of spin angular momentum aren't functions that canc take on any value given any polar/azimuthal angles, but rather just states(vectors), so we write the spin eigenvalue equations as

$$S^2 \left|s,m\right\rangle = \hbar^2 s(s+1) \left|s,m\right\rangle \quad \text{and} \quad S_z \left|s,m\right\rangle = \hbar m \left|s,m\right\rangle, \tag{6.73}$$

  where this m is different than the one associated with orbital angular momentum, but rarely if ever do both appear in the same equation/context, so it is normally enough to label them both as m. If a distinction needs to be made, I'll subscript it with the corresponding other eigenvalue, so this m would be m_s and the orbital one would be m_ℓ.

- It can also be shown that with $S_\pm \equiv S_x \pm iS_y$,

$$S_\pm \left|s,m\right\rangle = \hbar\sqrt{s(s+1) - m(m\pm 1)} \left|s,(m\pm 1)\right\rangle. \tag{6.74}$$

- Again, s (and therefore m) can take on half-integer values.

- The (arguably) most important case to consider is when $s = 1/2$, called "spin one-half". This admits $m = -1/2, +1/2$, so we have two possible states: $|\frac{1}{2},\frac{1}{2}\rangle$ and $|\frac{1}{2},-\frac{1}{2}\rangle$. It follows, then, that we can express any generic spin 1/2 state as a two component object called a **spinor**:

$$\chi = \begin{pmatrix} a \\ b \end{pmatrix} = a\chi_+ + b\chi_-, \tag{6.75}$$

  where χ_+ (corresponding to spin-up) and χ_- (corresponding to spin-down) are

$$\chi_+ = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \quad \text{and} \quad \chi_- = \begin{pmatrix} 0 \\ 1 \end{pmatrix}. \tag{6.76}$$

- Our operators, in this basis, are 2×2 matrices. For instance, since $S^2 \left|s,m\right\rangle = \hbar^2 s(s+1)\left|s,m\right\rangle$, with $s = 1/2$ then $S^2\chi_\pm = \frac{3}{4}\hbar^2\chi_\pm$, we can write S^2 as

$$S^2 = \begin{pmatrix} c & d \\ e & f \end{pmatrix}. \tag{6.77}$$

- Working things out using the equations for $S^2\chi_\pm$, we end up finding that

$$S^2 = \frac{3}{4}\hbar^2 \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{6.78}$$

- We can find quite easily that

$$S_z = \frac{\hbar}{2} \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.79}$$

- With our definitions of $S_\pm$, we can end up finding that

$$S_x = \frac{\hbar}{2} \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \text{and} \quad S_y = \frac{\hbar}{2} \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}. \tag{6.80}$$

- These all have a factor of $\hbar/2$, so we will say $\mathbf{S} = \hbar/2\boldsymbol{\sigma}$, where the σ's are called the **Pauli matrices**:

$$\sigma_x = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix}, \quad \sigma_y = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix}, \quad \text{and} \quad \sigma_z = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}. \tag{6.81}$$

7 Identical Particles

- For multiple particles, we have some simple generalizations. First, the wavefunction is now a function of all the positions of the particles: $\Psi(\{\mathbf{r}_n\}, t)$.
- The probabilistic interpretation is similar: now, the quantity $|\Psi(\{\mathbf{r}_n\}, t)|^2 \prod_{i=1}^{n} \mathrm{d}^3\mathbf{r}_i$ is the probability that *each particle* is contained in its infinitesimal volume element $\mathrm{d}^3\mathbf{r}_i$.
- The changes to the Schrodinger equation are relatively simple: the time evolution operator remains the same, but the Hamiltonian changes. Now, we sum all of the kinetic terms and the potential is a function of all the positions of all the particles:

$$i\hbar\frac{\partial\Psi}{\partial t} = \hat{H}\Psi = \left(-\frac{\hbar^2}{2m}\sum_{i=1}^{n}\boldsymbol{\nabla}_i^2 + V(\{\mathbf{r}_n\})\right). \tag{7.1}$$

- Just as before, if the potential is independent of time (which it is for this course), we can find stationary states

$$\Psi(\{\mathbf{r}_n\}, t) = \psi(\{\mathbf{r}_n\})e^{-iE\hbar/t}. \tag{7.2}$$

- Now, in an atom with atomic number Z (meaning there are Z protons, and if it is not an ion, Z electrons). We will consider the nucleus to be effectively stationary, which makes our work quite a bit easier.
- In this case, we will have the kinetic terms of the electrons, the potential between the nucleus and each electron, then the interactions among the electrons themselves:

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\boldsymbol{\nabla}_i^2 - \sum_{i=1}^{Z}\frac{Ze^2}{|\mathbf{R}-\mathbf{r}_i|} + \sum_{i<j}\frac{e^2}{|\mathbf{r}_i-\mathbf{r}_j|}, \tag{7.3}$$

  where the final term's sum serves to remove duplicates from our counting of potentials among the electrons.
- Equations like this are very hard to solve, but we can separate it into two special cases that makes them easier to solve. The first is if the particles don't interact, e.g. the last term in the above Hamiltonian will be zero. Therefore, we could write the potential $V(\{\mathbf{r}_n\}) = \sum_i V(\mathbf{r}_i)$. The Hamiltonian is now separable, so we will have n equations for each particle itself. The total energy of the system will then just be the sum of all the individual energies, and the total wavefunction will be a product of each individual wavefunction: $\Psi = \prod_i \psi_i(\mathbf{r}_i)e^{iE_i\hbar/t}$.
- However there is a problem with this: *we have assumed the particles are distinguishable.* Otherwise, what sense does it make to say that particle 1 is in state 1 if there is no way to tell them apart?
- To make this easier to consider, let's only take two particles. In general, since there is no way to tell them apart, we can have particle 1 (represented by position $\mathbf{r}_1$) in state 1 or it can be state 2, and similarly for particle 2. The general state of a particle is a linear combination of the two:

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2) \pm \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)]. \tag{7.4}$$

- The + corresponds to if the particles are bosons and the minus corresponds to if the particles are fermions.
- With this, it immediately follows that no two electrons (ignoring spin for a moment) can occupy the same state, because then, with $\psi_1 = \psi_2$, we have

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = A[\psi_1(\mathbf{r}_1)\psi_1(\mathbf{r}_2) - \psi_1(\mathbf{r}_2)\psi_2(\mathbf{r}_1)] = 0, \tag{7.5}$$

  so there's no wavefunction at all.

- Now including spin, we have that the *combination*(product) of the position wavefunction and spin state must be anti-symmetric: so the product $\psi(\mathbf{r}_1, \mathbf{r}_2)\chi(1,2)$ must remain anti-symmetric under exchange of particles.

Addition of Angular Momentum

- Now, say that we have two electrons. They can either be in the spin-up state $\left|\frac{1}{2}, \frac{1}{2}\right\rangle$ or spin-down state $\left|\frac{1}{2}, -\frac{1}{2}\right\rangle$. We can shorthand write these states as $|\uparrow\rangle$ and $|\downarrow\rangle$, respectively.
- Now, if we form a combined state, of the two electrons, we'd expect four possible combinations: $|\uparrow,\uparrow\rangle$, $|\uparrow,\downarrow\rangle$, $|\downarrow,\uparrow\rangle$, and $|\downarrow,\downarrow\rangle$. Now, the z-component of spin will just add, meaning that $m = 1$ for the first case, $m = 0$ for the middle two cases, and $m = -1$ for the last case. With these upper and lower limits on m, it follows that $s = 1$, but for a state of $s = 1/2$, we expect only *three* states with $m = 1$, $m = 0$, and $m = -1$, meaning we have an extra $m = 0$ state...
- To remedy this, let's take the $|\uparrow,\uparrow\rangle = |1,1\rangle$ state and apply the lowering operator. We have two individual states within this combined state, so the combined lowering operator $S_- = S_-^{(1)} + S_-^{(2)}$. Thus:

$$S_- |\uparrow,\uparrow\rangle = S_- |1,1\rangle = \left(S_-^{(1)} |\uparrow\rangle\right) |\uparrow\rangle + |\uparrow\rangle \left(S_-^{(2)} |\uparrow\rangle\right) \tag{7.6}$$

$$\hbar\sqrt{2}\, |1,0\rangle = \hbar \left(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\right) \tag{7.7}$$

$$|1,0\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\right). \tag{7.8}$$

- Therefore, there are three states with $s = 1$:

$$\begin{cases} |1,1\rangle & = |\uparrow,\uparrow\rangle, \\ |1,0\rangle & = \frac{1}{\sqrt{2}} \left(|\uparrow,\downarrow\rangle + |\downarrow,\uparrow\rangle\right), \\ |1,-1\rangle & = |\downarrow,\downarrow\rangle. \end{cases} \tag{7.9}$$

- It turns out, that if we apply the lowering operator again to $|1,0\rangle$, we get $|1,-1\rangle$, and if we apply the raising operator we return to $|1,1\rangle$, as expected. Additionally, applying the raising operator to $|1,1\rangle$ or the lowering operator to $|1,-1\rangle$ give zero, so it seems this works nicely.
- Now, there is nothing stopping a potential $s = 0$ state. This would admit only one state which would have $m = 0$. In fact, it seems almost natural to find another $m = 0$ state due to our double $m = 0$ from before. We just need to construct a state such that if we apply either raising or lowering operator results in zero. It turns out this is

$$|0,0\rangle = \frac{1}{\sqrt{2}} \left(|\uparrow,\downarrow\rangle - |\downarrow,\uparrow\rangle\right). \tag{7.10}$$

- The three $s = 1$ states form a **triplet** that is symmetric, and this single $s = 0$ state forms a **singlet**, than is anti-symmetric.

Note

- We covered next Helium, and some periodic table stuff which followed from the idea of no two electrons being able to occupy the same state. We can fit two into one position/energy state, but only so long as their spins are opposite. This leads to subsequent elements in the periodic table needing to push their electrons into higher states, called orbitals.
- Anyway, this is cool and all but I don't care to write it because it is hardly important.

8 Symmetries

- We say that a system has a *symmetry* under an action if the Hamiltonian remains unchanged under that action. For instance, the Hamiltonian will have *rotational symmetry* if it remains unchanged under a rotation.
- Let's consider a translation operator $\hat{T}(a)$ which has the effect

$$\hat{T}(a)\psi(x) = \psi'(x) = \psi(x-a). \tag{8.1}$$

- This is simple; how do we describe such a transformation on an operator $\hat{Q}$?
- We can determine this by noting that the expectation value of this operator should be the same regardless if we transform the wavefunction or if we transform the operator. With this,

$$\langle\psi'|\hat{Q}|\psi'\rangle = \langle\psi|\hat{Q}'|\psi\rangle \tag{8.2}$$
$$\langle\psi|\hat{T}^\dagger\hat{Q}\hat{T}|\psi\rangle = \langle\psi|\hat{Q}'|\psi\rangle\,, \tag{8.3}$$

  so

$$\boxed{\hat{Q}' = \hat{T}^\dagger\hat{Q}\hat{T}.} \tag{8.4}$$

- As an example, let's consider what is $\hat{x}'$?

$$\hat{x}'f(x) = [\hat{T}^\dagger(a)x\hat{T}(a)]f(x) \tag{8.5}$$
$$= \hat{T}(a)[xf(x-a)]. \tag{8.6}$$

  Since $xf(x-a)$ is another function of x, we can say that $\hat{x}' = \hat{x} + a$.

- Now, it turns out that momentum is the generator for translations, meaning

$$\hat{T}(a) = e^{-ia\hat{p}/\hbar}. \tag{8.7}$$

  From this definition, it is easy to see that $\hat{p}' = \hat{p}$, since any operator commutes with itself.

- With this, if the potential has a translational symmetry, then the Hamiltonian will remain unchanged:

$$\hat{H}' = \hat{T}^\dagger\hat{H}\hat{T} = \hat{H}. \tag{8.8}$$

- With a little bit of work, we can then find that in this case, the Hamiltonian and the translation operator commute, meaning that we can form simultaneous eigenstates.
- **Other symmetries for other transformations can be found in exactly the same way.**

9 Final Words

- I ended up getting quite lazy by the end of the semester. Stuff was also getting real slow and moderately easy since I have seen (at least some) fo this symmetry stuff before, so I stopped taking notes. In principle I'd look into the book and finish up, but I don't want to!