Week 2

The Schrödinger Equation

2.1 Particle-Wave Duality and Uncertainty Relations

10/4:
- Particle-wave duality (de Brogelie's original formulation):

$$\lambda\nu = c \qquad\qquad E = h\nu \qquad\qquad p = \frac{h}{\lambda}$$

- **Angular frequency**: The quantity $\omega = 2\pi r$.
- **Wavenumber**: The quantity $k = 2\pi/\lambda$.
- We can create a symmetrical formulation of the de Broglie relation using these new quantities:

$$E = \hbar\omega \qquad\qquad p = \hbar k$$

- What is the wave that we might associate with a de Broglie particle?

$$\Psi(x) = A\mathrm{e}^{ikx - i\omega t}$$

- Probability:
  - Classically, such a wave might be associated with EM radiation hitting a surface with intensity $I = |\Psi(x)|^2 = \Psi(x)\Psi^*(x)$.
  - As soon as we associate a particle (photon) with the wave, the intensity may be re-interpreted as the number of particles reaching the surface or the probability of a particle being at the surface.
  - Thus, the probability of finding a particle at the surface becomes $|\Psi(x)|^2$, as well.
- Following de Broglie, we also associate waves with particles such as electrons.
  - With the association of light as a particle, the particle wave duality leads to the appearance of probability.
- What is the probability of finding the particle at the origin?

$$\begin{aligned} Pr &= \left|A\mathrm{e}^{ik\cdot 0}\right|^2 \\ &= |A|^2 \end{aligned}$$

  - Since the probability is not dependent on position, it is the same everywhere.
  - We also run into issues **normalizing** this unbounded wavefunction.

  - We know this particle's momentum exactly, but we know nothing about its position.
- **Normalizing** (a wavefunction): Guaranteeing that the integral for the entire wavefunction is equal to 1.
- **Free particle**: A particle that does not have constraints on where it is more likely to be.
- Heisenberg's uncertainty relations are formalized in terms of matrix mechanics.
  - We can Fourier transform the wave function of particle to convert it from a function of position to a function of momentum.
  - The Fourier transform will yield one spike at $\hbar k$ and will be 0 everywhere else — just like the Dirac delta function.
  - Thus,
$$\Psi(p) = \delta(p - \hbar k)$$
- Consider a Gaussian wave packet at $p = 0$. Then
$$\phi(p) = C\mathrm{e}^{-\frac{p^2}{2(\Delta p)^2}}$$
  - Δp is the standard deviation of the Gaussian/width of the distribution. It is a constant such that the probability drops to 1/e of its maximum at $p = 0$.
- With the Fourier Transform of $\Psi(p)$, we obtain
$$\Psi(x) = D\mathrm{e}^{-\frac{(\Delta p)^2 x^2}{2\hbar^2}}$$
  - Thus, a Gaussian quantum function produces a Gaussian position function via an FT as well, i.e.,
$$\Psi(x) = D\mathrm{e}^{-\frac{x^2}{2(\Delta x)^2}}$$
- Now if we set the last two equations equal to each other, we get
$$\begin{aligned}\frac{(\Delta p)^2}{2\hbar^2} &= \frac{1}{2(\Delta x)^2}\\ (\Delta p)^2(\Delta x)^2 &= \hbar^2\\ \Delta p\Delta x &= \hbar = \frac{h}{2\pi}\end{aligned}$$
  - This implies that the spread of the Gaussian in momentum times the spread of the Gaussian in position is a constant.
  - If we make one Gaussian wave packet more specific, the other gets more spread out, and vice versa.
  - Note that the above equality does *satisfy* the Heisenberg uncertainty principle, but it is not it itself.

2.2 The Schrödinger Equation and Particle in a Box

10/6:
- Review:
  - de Broglie describes an electron as a free particle.
$$\Psi(x) = A\mathrm{e}^{ikx}$$
  - We can only observe the real part, but being able to access the complex part is important in quantum mechanics.

- Schrödinger was on vacation in the Swiss Alps with his mistress when he derived the wave equation.
  - Schrödinger realized that
    $$\begin{aligned}\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x} &= Aik\mathrm{e}^{ikx}\\ -i\hbar\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x} &= Ap\mathrm{e}^{ikx}\\ &= p\Psi(x)\end{aligned}$$
  - Let's introduce operators in quantum mechanics and let $\hat{p}$ be an operator that when it acts on $\Psi(x)$, it gives the above. In other words,
    $$\hat{p} = -i\hbar\frac{\mathrm{d}}{\mathrm{d}x}$$
  - Thus,
    $$\hat{p}\Psi(x) = p\Psi(x)$$
  - But energy is more important than momentum, so let's introduce an energy operator $\hat{T}$ related to $\hat{p}$ by
    $$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}$$
    since $E = mv^2/2 = p^2/(2m)$.
  - Thus, we have
    $$\hat{T}\Psi(x) = \frac{p^2}{2m}\Psi(x)$$
  - It follows from classical physics that the total energy operator $\hat{H}$ (the Hamiltonian) is the sum of the kinetic and potential energy operators, i.e., $\hat{H} = \hat{T} + \hat{V}$. Therefore, we must have
    $$\hat{H}\Psi(x) = E\Psi(x)$$
    and that is the Schrödinger equation.
- The particle in a box is like a single electron in a one-dimensional chamber that runs from $-a$ to a with $L = 2a$ (Schrödinger figured this out a few days later, still in the Swiss Alps).
  - The walls are infinite and have infinite potential.
  - We need the boundary condition, though, to be able to solve a differential equation like the Schrödinger equation.
    - Fortunately, we know that at $|x| = a$, we have $\Psi(\pm a) = 0$.
    - Another important point is that $\mathrm{d}\Psi(x)/\mathrm{d}x$ at a is discontinuous.
  - So we have that
    $$\begin{aligned}-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi_n(x) &= E_n\Psi_n(x)\\ \frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi(x) &= -k^2\Psi(x)\end{aligned}$$
    where
    $$k = \sqrt{\frac{2mE}{\hbar^2}}$$
  - The solution of the differential equation will be of the form
    $$\Psi(x) = A\cos(kx) + B\sin(kx)$$

- Boundary conditions 1 and 2, respectively:

$$\begin{aligned} 0 &= \Psi(a) \\ &= A\cos(ka) + B\sin(ka) \end{aligned} \qquad \begin{aligned} 0 &= \Psi(-a) \\ &= A\cos(ka) - B\sin(ka) \end{aligned}$$

- Adding/subtracting the two equations yields

$$A\cos(ka) = 0 \qquad B\sin(ka) = 0$$

- We satisfy these equations with either of 2 classes of nontrivial solutions (the trivial solution being $a = 0$).
  1. $B = 0$ and $\cos(ka) = 0$, i.e., $k_n = \frac{n\pi}{2a}$ for $n \in 2\mathbb{N} + 1$.
  2. $A = 0$ and $\sin(ka) = 0$, i.e., $k_n = \frac{n\pi}{2a}$ for $n \in 2\mathbb{N}$.
- Thus, either

$$\Psi_n(x) = \frac{1}{\sqrt{a}} \cos\left(\frac{n\pi x}{2a}\right)$$

  for $n \in 2\mathbb{N} + 1$ are the **even solutions** (because cosine is an even function), and

$$\Psi_n(x) = \frac{1}{\sqrt{a}} \sin\left(\frac{n\pi x}{2a}\right)$$

  for $n \in 2\mathbb{N}$ are the **odd solutions** (because sine is an odd function).
- Note that we derive the $1/\sqrt{a}$ coefficient by normalizing $\Psi(x)$ with

$$\int_{-a}^{a} |\Psi(x)|^2 \,\mathrm{d}x = \int_{-a}^{a} \Psi^*(x)\Psi(x) = 1$$

- The energies come out to

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{\hbar^2}{8m} \cdot \frac{\pi^2 n^2}{a^2}$$

  with the substitution $k_n = \frac{n\pi}{2a}$.
  - Note that this means that the particle becomes more discrete the smaller the box gets (as uncertainty in position goes down, it acts more and more quantum mechanically).

2.3 Potential Step

10/8: • Particle in a box:

- For $n = 1$, the potential is defined by one hump of a sine wave.
- For $n = 2$, the potential is defined by two humps.
- The number of nodes is equal to the principal quantum number minus 1.
- We have

$$E_n = \frac{\hbar^2}{8m} \frac{\pi^2 n^2}{a^2}$$

  for $n \in \mathbb{N}$.
- By the Heisenberg uncertainty relationship, we must have $E_1 > 0$. In other words, the **zero-point energy** arises from the UR.
- Trend wrt. a: As $a \to \infty$, all of the energies become degenerate.
- Trend wrt. m: As $m \to \infty$, $E_n \to 0$ as well.
  - In other words, as $m \to \infty$, the particle behaves more classically!
  - The zero-point energy also disappears as $a \to \infty$.

- **Zero-point energy**: The lowest possible energy a quantum mechanical system may have.
- All of that information comes from the Schrödinger equation, so we now know much more than we used to.
- Free particle vs. particle in a box:
  - For a free particle, we have $\Psi(x) = \mathrm{e}^{ikx}$. Boundary condition was a circle (as per the Bohr model).
  - In the particle in a box, we weed out all of the free particle solutions that don't match the boundary conditions. And the only solutions that match the boundary conditions are the ones that have integers for the quantum number n.
  - The only constraint is that you can retain more particles the bigger the box gets; this is why the particle gets more quantum mechanical as you shrink the box.
- **Potential step**: Let the energy E be 0 up until the origin, where it steps up to potential V_0.

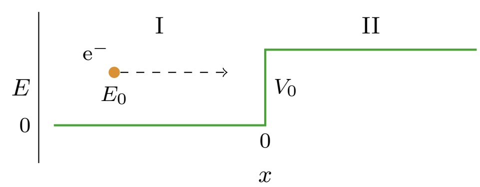

Figure 2.1: Potential step.

  - We shoot a particle at a potential wall with energies varying from below the top to above the top.
- In classical mechanics, we have

$$E = \frac{p^2}{2m} + V$$

  - In region I, there's no potential, so the total energy is all kinetic. The particle is moving with momentum $p_{\mathrm{I}} = \sqrt{2mE}$.
  - In region II, the particle is moving with momentum $p_{\mathrm{II}} = \sqrt{2m(E-V)}$.
    - If $E_0 < V$, the particle *never* passes from region I $\to$ II.
    - If $E_0 > V$, the particle *always* passes from I $\to$ II, but has less KE in II than I[1].
- Quantum particle motion:

$$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi(x) + V(x)\Psi(x) = E\Psi(x)$$
$$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi(x) + k^2\Psi(x) = 0$$

  where $k = \sqrt{2m(E-V)/\hbar^2}$.
  - The total wave function will be the sum of the LCAOs that fit the boundary condition.
  - Our general solution has two parts:

$$\Psi_{\mathrm{I}}(x) = A\mathrm{e}^{i\alpha x} + B\mathrm{e}^{-i\beta x} \qquad \Psi_{\mathrm{II}}(x) = C\mathrm{e}^{i\alpha x} + D\mathrm{e}^{-i\beta x}$$

  - Two energy cases: $E > V_0$ and $E < V_0$.

[1]Note that the classical resolution to the case $E = V_0$ is that the particle never has $E_0 = V$; it always has energy ϵ above or ϵ below V. However, in some sense, there *is* another answer: Classical mechanics is not an "accurate" reflection of reality, and this is a place where it shows. Indeed, we *need* quantum mechanics to treat this case.

- $E > V_0$:
  - We must maintain the continuity of the $\Psi(x)$ and $\mathrm{d}\Psi(x)/\mathrm{d}x$ at $x = 0$. This yields

$$A + B = C + D \qquad\qquad i\alpha(A - B) = i\beta(C - D)$$

  - It follows that

$$A = \frac{C(\alpha+\beta)}{2\alpha} + \frac{D(\alpha-\beta)}{2\alpha} \qquad\qquad B = \frac{C(\alpha-\beta)}{2\alpha} + \frac{D(\alpha+\beta)}{2\alpha}$$

  - Assume that the particles only travel from left to right in II, i.e., $D = 0$.
  - The flux of the particle: The probability of the particle going left to right in region I is $|A|^2$. Thus, since the incident flux factors in the speed v_I of the particle, the incident flux is $v_{\mathrm{I}}|A|^2$. Similarly, the transmitted flux of the particle is $v_{\mathrm{II}}|C|^2$.
  - Consequently, the reflected flux of the particles is

$$R = \frac{c|B|^2}{c|A|^2} = \frac{|B|^2}{|A|^2} = \frac{(\alpha-\beta)^2}{(\alpha+\beta)^2}$$

    Note that the speed of the particle (the speed of light, c) is the same in both regions.
  - Conclusion: There is a probability of reflection *even when* $E_0 > V_0$, disagreeing with classical mechanics.
  - Fraction of transmitted particles:

$$T = \frac{v_{\mathrm{II}}}{v_{\mathrm{I}}}\frac{|C|^2}{|A|^2} = \frac{4\alpha\beta}{(\alpha+\beta)^2}$$

- $E < V_0$:
  - The continuity of $\Psi(x)$ and $\Psi'(x)$ at $x = 0$ again gives us

$$A + B = C + D \qquad\qquad i\alpha(A - B) = i\beta(C - D)$$

  - But since we have

$$\beta = \frac{\sqrt{2m(E - V_0)}}{\hbar}$$

    and $E - V_0 < 0$, β will be a complex number.
  - Thus, to treat the real and complex portions of β separately, we define β_2 to be a real number.
  - Consequently, we may write

$$R = \frac{|B|^2}{|A|^2} = \frac{|\alpha-\beta|^2}{|\alpha+\beta|^2} = \frac{|\alpha - i\beta_2|^2}{|\alpha + i\beta_2|^2} = \frac{\alpha^2+\beta_2^2}{\alpha^2+\beta_2^2} = 1$$

  - Conclusion: When the energy of the particle is less than the energy of the potential, even quantum mechanics predicts total reflection. However, there's still something subtle happening.
  - Let's look at the wave function in region II:

$$\Psi_{\mathrm{II}} = C\mathrm{e}^{i\beta x} = C\mathrm{e}^{i(i\beta_2)x} = C\mathrm{e}^{-\beta_2 x}$$

    where $\beta_2 > 0$ by definition.

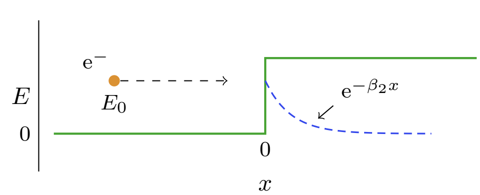

Figure 2.2: Quantum tunneling.

- Thus, even though the particle is reflected 100%, it has some probability of going through the step, namely a probability that decays exponentially the farther you go into the wall.
- This is **quantum tunneling**.
- The particle can't ever get to ∞, so that's why $T = 0$, but it can go into the wall for a little bit, just a sec.

2.4 MathChapter B: Probability and Statistics

10/10:

- "Consider some experiment, such as the tossing of a coin or the rolling of a die, that has n possible outcomes, each with probability p_j, where $j = 1, 2, \ldots, n$" (McQuarrie & Simon, 1997, p. 63).
- If the experiment is repeated indefinitely, we intuitively expect that for each $j = 1, \ldots, n$

$$p_j = \lim_{N\to\infty} \frac{N_j}{N}$$

  where N_j is the number of times that the event j occurs and N is the total number of repetitions of the experiment.
- The fact that $0 \leq N_j \leq N$ implies that $0 \leq p_j \leq 1$ by the above condition.
- **Certainty**: An event j such that $p_j = 1$.
- **Impossibility**: An event j such that $p_j = 0$.
- **Normalization condition**: The result that

$$\sum_{j=1}^{n} p_j = 1$$

  - This follows from the fact that $\sum_{j=1}^{n} N_j = N$ and the above.
  - The normalization condition expresses the idea that "the probability that some event occurs is a certainty" (McQuarrie & Simon, 1997, p. 64).
- **Average** (of x): The following quantity, where we associate some number x_j with each outcome j. *Also known as* **mean** (of x). *Denoted by* $\langle \boldsymbol{x} \rangle$. *Given by*

$$\langle x \rangle = \sum_{j=1}^{n} x_j p_j = \sum_{j=1}^{n} x_j p(x_j)$$

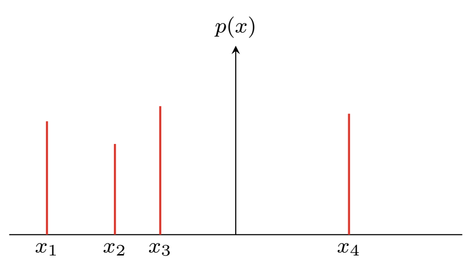

Figure 2.3: The discrete probability frequency function.

  - It is helpful to interpret a probability distribution like p_j as a distribution of a unit mass along the x-axis in a discrete manner such that p_j is the fraction of mass located at the point x_j.
  - According to this interpretation, the average value of x is the center of mass of this system.

- **Second moment** (of the distribution $\{p_j\}$): The following quantity.

$$\langle x^2\rangle = \sum_{j=1}^{n} x_j^2 p_j$$

  - Note that $\langle x^2\rangle \neq \langle x\rangle^2$.
  - Analogous to the moment of inertia.
- The next quantity is physically more interesting than the second moment.
- **Second central moment**: The following quantity. *Also known as* **variance**. *Denoted by* $\boldsymbol{\sigma_x^2}$. *Given by*

$$\sigma_x^2 = \langle (x-\langle x\rangle)^2\rangle = \sum_{j=1}^{n}(x_j-\langle x\rangle)^2 p_j$$

  - $\sigma_x^2 \geq 0$ because it is a sum of positive terms.
  - An alternate form of σ_x^2:

$$\begin{aligned}
\sigma_x^2 &= \sum_{j=1}^{n}(x_j-\langle x\rangle)^2 p_j\\
&= \sum_{j=1}^{n}(x_j^2-2\langle x\rangle x_j+\langle x\rangle^2)-p_j\\
&= \sum_{j=1}^{n}x_j^2 p_j - 2\langle x\rangle\sum_{j=1}^{n}x_j p_j + \langle x\rangle^2\sum_{j=1}^{n}p_j\\
&= \langle x^2\rangle - 2\langle x\rangle\cdot\langle x\rangle + \langle x\rangle^2\cdot 1\\
&= \langle x^2\rangle - \langle x\rangle^2
\end{aligned}$$

  - If $\sigma_x^2 = 0$ or $\langle x\rangle^2 = \langle x^2\rangle$, then we must have $x_j = \langle x\rangle$ for all j, i.e., the event is not really probabilistic because the event j occurs on every trial.
- **Standard deviation**: The positive square root of the variance. *Denoted by* $\boldsymbol{\sigma_x}$.
- Both the standard deviation and the variance are measures of the spread of the distribution about its mean.
- We now step into continuous probability distributions.
- **Linear mass density**: The quantity $\rho(x)$ defined by

$$\mathrm{d}m = \rho(x)\,\mathrm{d}x$$

  where $\mathrm{d}m$ is the fraction of the mass lying between x and $x+\mathrm{d}x$.
- It follows that the probability that, for example, a particle lies between positions x and $x+\mathrm{d}x$ in a box is

$$\text{Prob}(x, x+\mathrm{d}x) = p(x)\,\mathrm{d}x$$

- Therefore,

$$\text{Prob}(a\leq x\leq b) = \int_a^b p(x)\,\mathrm{d}x$$

- Furthermore, the continuous normalization condition becomes

$$\int_{-\infty}^{\infty} p(x)\,\mathrm{d}x = 1$$

- We may also analogously define

$$\langle x\rangle = \int_{-\infty}^{\infty} xp(x)\,\mathrm{d}x \qquad \langle x^2\rangle = \int_{-\infty}^{\infty} x^2p(x)\,\mathrm{d}x \qquad \sigma_x^2 = \int_{-\infty}^{\infty} (x-\langle x\rangle)^2p(x)\,\mathrm{d}x$$

- **Gaussian distribution**: The most commonly occuring and the most important continuous probability distribution. *Given by*

$$p(x)\,\mathrm{d}x = c\mathrm{e}^{-x^2/2a^2}\,\mathrm{d}x$$

  - Note that the normalization condition implies that

$$c = \frac{1}{\sqrt{2\pi a^2}}$$

  - We can also prove that

$$\sigma_x = a$$

  - Thus, the standard notation for a normalized Gaussian distribution function is

$$p(x)\,\mathrm{d}x = \frac{1}{\sqrt{2\pi\sigma_x^2}}\mathrm{e}^{-x^2/2\sigma_x^2}\,\mathrm{d}x$$

  - Note that as σ_x gets smaller, the bell curves become narrower and taller, and vice versa as it gets larger.
  - A more general form (one that accounts for a center at $x = \langle x\rangle$ as opposed to just $x = 0$) is

$$p(x)\,\mathrm{d}x = \frac{1}{\sqrt{2\pi\sigma_x^2}}\mathrm{e}^{-(x-\langle x\rangle)^2/2\sigma_x^2}\,\mathrm{d}x$$