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:

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

- 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 $1/\mathrm{e}$ 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

$$\frac{(\Delta p)^2}{2\hbar^2} = \frac{1}{2(\Delta x)^2}$$
$$(\Delta p)^2(\Delta x)^2 = \hbar^2$$
$$\Delta p \Delta x = \hbar = \frac{h}{2\pi}$$

    – 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

  $$\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x} = Aik\mathrm{e}^{ikx}$$

  $$-i\hbar\frac{\mathrm{d}\Psi(x)}{\mathrm{d}x} = Ap\mathrm{e}^{ikx}$$

  $$= p\Psi(x)$$

  - 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

  $$-\frac{\hbar^2}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi_n(x) = E_n\Psi_n(x)$$

  $$\frac{\mathrm{d}^2}{\mathrm{d}x^2}\Psi(x) = -k^2\Psi(x)$$

  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:

$$0 = \Psi(a) \qquad\qquad\qquad\qquad 0 = \Psi(-a)$$
$$= A\cos(ka) + B\sin(ka) \qquad\qquad\qquad = A\cos(ka) - B\sin(ka)$$

– Adding/subtracting the two equations yields

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

– 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).