

Week 2

The Schrödinger Equation

2.1 Particle-Wave Duality and Uncertainty Relations

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

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

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

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

- What is the wave that we might associate with a de Broglie particle? Start with a completely general oscillator Ae^{iy} (are we also using complex coordinates to rigorously describe a circular Bohr orbit??), and substitute in the periodicity conditions from the classical wave equation, i.e., $kx - \omega t$ to get

$$\psi(x) = Ae^{i(kx - \omega t)}$$

- Probability:
 - By the classical wave power equation, 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?

$$\begin{aligned} \text{Prob} &= |Ae^{ik \cdot 0}|^2 \\ &= |A|^2 \end{aligned}$$

- 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

$$\phi(p) = Ce^{-\frac{p^2}{2(\Delta p)^2}}$$

- 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

$$\psi(x) = De^{-\frac{(\Delta p)^2 x^2}{2\hbar^2}}$$

- Thus, a Gaussian quantum function produces a Gaussian position function via an FT as well, i.e.,

$$\psi(x) = De^{-\frac{x^2}{2(\Delta x)^2}}$$

- 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.

$$\psi(x) = Ae^{ikx}$$

- 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

$$\begin{aligned}\frac{d\psi(x)}{dx} &= Aike^{ikx} \\ -i\hbar \frac{d\psi(x)}{dx} &= Ape^{ikx} \\ &= p\psi(x)\end{aligned}$$

- 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,

$$\hat{p} = -i\hbar \frac{d}{dx}$$

- 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

$$\hat{T} = \frac{\hat{p}^2}{2m} = \frac{-\hbar^2}{2m} \frac{d^2}{dx^2}$$

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 $d\psi(x)/dx$ at a is discontinuous.
 - So we have that

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

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:

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

- 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

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

- 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 $a \rightarrow \infty$, all of the energies become degenerate.

- Trend wrt. m : As $m \rightarrow \infty$, $E_n \rightarrow 0$ as well.
 - In other words, as $m \rightarrow \infty$, the particle behaves more classically!
 - The zero-point energy also disappears as $a \rightarrow \infty$.
- **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 $\psi(x) = e^{ikx}$. 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 .

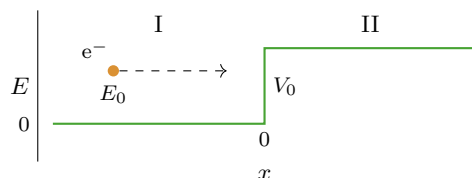


Figure 2.1: Potential step.

- 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 $p_I = \sqrt{2mE}$.
 - In region II, the particle is moving with momentum $p_{II} = \sqrt{2m(E - V)}$.
 - If $E_0 < V$, the particle *never* passes from region I \rightarrow II.
 - If $E_0 > V$, the particle *always* passes from I \rightarrow II, but has less KE in II than I^[1].
- Quantum particle motion:

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

$$\frac{d^2}{dx^2} \psi(x) + k^2 \psi(x) = 0$$

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:

$$\psi_I(x) = Ae^{i\alpha x} + Be^{-i\alpha x}$$

$$\psi_{II}(x) = Ce^{i\beta x} + De^{-i\beta x}$$

¹Note that the classical resolution to the case $E = V_0$ is that the particle never has $E = V_0$; 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.

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

- We must maintain the continuity of the $\psi(x)$ and $d\psi(x)/dx$ at $x = 0$. This yields

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

- It follows that

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

- 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 $v_I|A|^2$. Similarly, the transmitted flux of the particle is $v_{II}|C|^2$.
- 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:

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

- $E < V_0$:

- The continuity of $\psi(x)$ and $\psi'(x)$ at $x = 0$ again gives us

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

- But since we have

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

and $E - V_0 < 0$, β will be an imaginary number.

- Thus, we define β_2 to be the real number such that $\beta = i\beta_2$.
- 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:

$$\psi_{II} = Ce^{i\beta x} = Ce^{i(i\beta_2)x} = Ce^{-\beta_2 x}$$

where $\beta_2 > 0$ by definition.

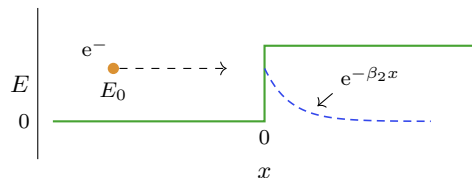


Figure 2.2: Quantum tunneling.

- 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 Chapter 2: The Classical Wave Equation

From McQuarrie and Simon (1997).

1/3/23:

- Goal.
 - Ground the study of the Schrödinger equation (a PDE) with an easily visualized and highly related example from classical physics. Introduce the mathematics required for such problems and show how it relates to physical reality.
- Consider a uniform vibrating string stretched between two fixed points at $x = 0, l$.
 - At position x and time t , we say that the string is displaced $u(x, t)$ from its equilibrium position.
- **Amplitude** (of a string): The maximum displacement of the string from its equilibrium horizontal position.
- It can be shown — see Figure 15.2 and the associated discussion in Labalme (2021) — that $u(x, t)$ satisfies the **classical wave equation**.
- **Classical wave equation**: The following linear partial differential equation. *Given by*

$$\frac{\partial^2 u(x, t)}{\partial x^2} = \frac{1}{v^2} \frac{\partial^2 u(x, t)}{\partial t^2}$$

- **Partial differential equation**: An equation in which the unknown occurs in partial derivatives. *Also known as PDE.*
- **Independent variable**: A variable in a PDE such as x or t .
- **Dependent variable**: A variable in a PDE that depends on the independent variables, such as $u(x, t)$.
- **Linear differential equation**: A differential equation in which the dependent variable and its derivatives appear only to the first power, and in which there are no cross terms.
- Additional physical conditions $u(x, t)$ must satisfy.
 - The ends of the string are held fixed. Thus, the amplitude at these two points is always zero. Mathematically,

$$u(0, t) = 0$$

$$u(l, t) = 0$$

for all t .

- **Boundary condition**: A condition that specifies the behavior of the dependent variable at the boundaries.
 - The above additional physical conditions are boundary conditions.
 - In general, PDEs are solved subject to boundary conditions, the nature of which derives from physical considerations.
- **Separation of variables**: The method needed to solve the classical wave equation, the Schrödinger equation, and many other PDEs that arise in physical chemistry. *Procedure*

1. Assume that the dependent variable factors into the product of functions of its independent variables^[2].
 2. Substitute in the **ansatz** and algebraically rearrange the equation to gather all instances of each independent variable into distinct additive terms.
 3. Set each term equal to the **separation constant**.
 - This is allowed because the equality derived in step two must be valid under any variation of the independent variables. But since the *independent* variables can be varied independently, we can move any one of them around while holding the others constant and the equality must be preserved; thus, since the other terms are certainly constant under no variation, the term being varied must be constant as well.
 - This will yield one **ordinary differential equation** for each variable. These can be solved using knowledge from previous calculus courses.
- **Ansatz:** The assumed form of an unknown function.
 - **Separation constant:** A to-be-determined constant.
 - **Ordinary differential equation:** An equation in which the unknown occurs in ordinary derivatives. *Also known as ODE.*
 - Applying the method of separation of variables to the classical wave equation.
 1. Assume $u(x, t)$ factors into a function $X(x)$ of x times a function $T(t)$ of t , that is,

$$u(x, t) = X(x)T(t)$$

2. Substitute and rearrange.

$$\begin{aligned}\frac{\partial^2 X(x)T(t)}{\partial x^2} &= \frac{1}{v^2} \frac{\partial^2 X(x)T(t)}{\partial t^2} \\ T(t) \frac{d^2 X(x)}{dx^2} &= \frac{1}{v^2} X(x) \frac{d^2 T(t)}{dt^2} \\ \frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} &= \frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2}\end{aligned}$$

3. Let K denote the separation constant. Then we obtain the following two ODEs.

$$\begin{aligned}\frac{1}{X(x)} \frac{d^2 X(x)}{dx^2} &= K & \frac{1}{v^2 T(t)} \frac{d^2 T(t)}{dt^2} &= K \\ \frac{d^2 X(x)}{dx^2} - KX(x) &= 0 & \frac{d^2 T(t)}{dt^2} - Kv^2 T(t) &= 0\end{aligned}$$

- In particular, these equations are **linear differential equations with constant coefficients**, which can be solved as follows.
- Interrogating the resultant ODEs.
 - K is yet to be determined. Let's see what the solutions look like for different values.
 - $K = 0$: This yields the solutions

$$X(x) = a_1 x + b_1$$

$$T(t) = a_2 t + b_2$$

where a_1, a_2, b_1, b_2 are constants of integration.

²In the domain of differential equations, we can always assume that the solution has any form we want, and then solve to find all solutions *of this form*. However, this set of solution may not encapsulate *all* solutions, i.e., it may not be the *general solution*.

- Applying the boundary conditions, we learn that

$$u(0, t) = X(0)T(t) = 0 \qquad u(l, t) = X(l)T(t) = 0$$

- We now divide into two cases.
 - If $T(t) = 0$ for all t , then the solution is $u(x, t) = X(x) \cdot 0 = 0$. This is referred to as the **trivial solution**, and it corresponds to the string at rest.
 - If $T(t) \neq 0$ for some T , then $X(0) = X(l) = 0$, which implies that $a_1 = b_1 = 0$ (think about the functional form algebraically). It follows that $X(x) = 0 \cdot x + 0 = 0$ for all x , and we obtain the trivial solution again.
- $K > 0$: Every (linearly independent) solution to equations of this type is of the form $e^{\alpha x}$ ^[3]. Substituting into the ODE describing $X(x)$, we obtain

$$(\alpha^2 - K^2)X(x) = 0$$

- Assuming $X(x)$ is nontrivial, we must have $\alpha^2 - K^2 = 0$, or $\alpha = \pm K$.
- Thus, there are two solutions: $X(x) = e^{Kx}, e^{-Kx}$.
- It follows from the fact that the relevant ODE is *linear* that

$$X(x) = c_1 e^{Kx} + c_2 e^{-Kx}$$

is also a solution.

- McQuarrie and Simon (1997) attempts to justify why the above is the general solution; a more rigorous explanation can be found in Labalme (2022).
- McQuarrie and Simon (1997) provides further examples of ODEs that can be solved by the ansatz $e^{\alpha x}$ and factoring a binomial, as well as solving for c_1, c_2 using initial conditions.

2.5 MathChapter B: Probability and Statistics

From McQuarrie and Simon (1997).

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 $j = 1, 2, \dots, n$ ” (McQuarrie & Simon, 1997, p. 63).
- If the experiment is repeated indefinitely, we intuitively expect that for each $j = 1, \dots, n$

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

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.

³See Labalme (2022) for more.

- 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 $\langle x \rangle$. Given by

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

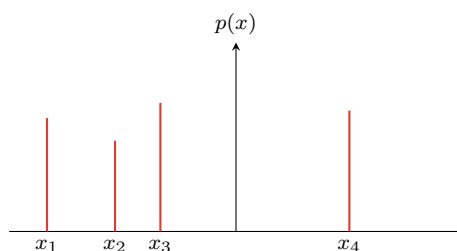


Figure 2.3: The discrete probability frequency function.

- 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 σ_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 σ_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

$$dm = \rho(x) dx$$

where dm is the fraction of the mass lying between x and $x + dx$.

- It follows that the probability that, for example, a particle lies between positions x and $x + dx$ in a box is

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

- Therefore,

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

- Furthermore, the continuous normalization condition becomes

$$\int_{-\infty}^{\infty} p(x) dx = 1$$

- We may also analogously define

$$\langle x \rangle = \int_{-\infty}^{\infty} xp(x) dx \quad \langle x^2 \rangle = \int_{-\infty}^{\infty} x^2 p(x) dx \quad \sigma_x^2 = \int_{-\infty}^{\infty} (x - \langle x \rangle)^2 p(x) dx$$

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

$$p(x) dx = ce^{-x^2/2a^2} dx$$

- 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

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

- 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

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

2.6 Chapter 3: The Schrödinger Equation and a Particle In a Box

From McQuarrie and Simon (1997).

- **Schrödinger equation:** The fundamental equation of quantum mechanics. A differential equation whose solution $\psi(x)$ describes a particle of mass m moving in a potential field described by $V(x)$. Given by

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

- **Wave function:** A solution to the Schrödinger equation. A measure of the amplitude of the matter wave. Denoted by $\psi(x)$
- **Stationary-state wave function:** A solution to the time-independent Schrödinger equation.
- **Particle in a box:** A system consisting of a free particle of mass m that is restricted to lie along a one-dimensional interval of length a .
- **Spatial amplitude** (of a wave): The function $\psi(x)$ of position that serves as a coefficient to a time-dependent wave function.
- **Operator:** A symbol that tells you to do something to whatever follows the symbol. Denoted by a capital letter with a carat over it.
- **Linear operator:** An operator \hat{A} such that

$$\hat{A}[c_1f_1(x) + c_2f_2(x)] = c_1\hat{A}f_1(x) + c_2\hat{A}f_2(x)$$

where c_1, c_2 are (possibly complex) constants.

- **Eigenvalue problem:** The problem of determining $\phi(x)$ and a given \hat{A} such that

$$\hat{A}\phi(x) = a\phi(x)$$

- **Eigenfunction:** The function $\phi(x)$ in an eigenvalue problem.
- **Eigenvalue:** The constant a in an eigenvalue problem.
- **Hamiltonian operator:** The following operator. Denoted by \hat{H} . Given by

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x)$$

- The substitution of the Hamiltonian operator into the Schrödinger equation allows us to formulate the Schrödinger equation as an eigenvalue problem.
 - The wave function then becomes the eigenfunction and the energy, the eigenvalue of the Hamiltonian operator.

- **Kinetic energy operator:** The following operator. Denoted by \hat{K}_x . Given by

$$\hat{K}_x = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

- Defined by taking $V(x) = 0$ in the Hamiltonian.

- **Momentum operator:** The following operator. Denoted by \hat{P}_x .

$$\hat{P}_x = -i\hbar \frac{d}{dx}$$

- Defined by applying $K = p^2/2m$ to the kinetic energy operator to get

$$\hat{P}_x^2 = -\hbar^2 \frac{d^2}{dx^2}$$

and then (noting that we define the square of an operator to be equivalent to applying the same operator successively) factoring the above into

$$\hat{P}_x^2 = \hat{P}_x \hat{P}_x = -\hbar^2 \frac{d^2}{dx^2} = \left(-i\hbar \frac{d}{dx}\right) \left(-i\hbar \frac{d}{dx}\right)$$

- **Free particle:** A particle that experiences no potential energy, i.e., a particle for which $V(x) = 0$.
- When solving the particle in a box, we say that $\psi(x)$ represents the the amplitude of the particle in some sense. More specifically, since the intensity of a wave is the square of the magnitude of the amplitude, we write that the “intensity of the particle” is proportional to $\psi^*(x)\psi(x)$.
 - Born, a German physicist working in scattering theory, formalized this by saying that $\psi^*(x)\psi(x) dx$ is the “probability that the particle is located between x and $x + dx$ ” (McQuarrie & Simon, 1997, p. 80).
- Schrödinger’s quantization of energy arises naturally from his equation and the boundary conditions, as opposed to having to be postulated as in Bohr’s model.
- McQuarrie and Simon (1997) use the free-particle model to crudely explain the absorption spectrum of butadiene.
- **Normalized** (wave function): A wave function of the form

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a}$$

- “Because the Hamiltonian operator is a linear operator, if ψ is a solution to $\hat{H}\psi = E\psi$, then any constant, say A , times ψ is also a solution, and A can always be chosen to produce a normalized solution to the Schrödinger equation” (McQuarrie & Simon, 1997, p. 84).
- **Correspondence principle:** Quantum mechanical results and classical mechanical results tend to agree in the limit of large quantum numbers.
- Applying the statistical principles to the particle in a box, we can calculate that

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

- Calculating the average energy or momentum:
 - To calculate the average value of the physical quantity associated with an operator, we sandwich the operator between a wave function $\psi_n(x)$ and its complex conjugate $\psi_n^*(x)$.
 - This will be formalized later, but for now, we assume that

$$\langle s \rangle = \int \psi_n^*(x) \hat{S} \psi_n(x) dx$$

where \hat{S} is the quantum-mechanical operator associated with the physical quantity s , and $\langle s \rangle$ is the average value of s in the state described for the wave function.

- For example, the average momentum of a particle in a box in the state described by $\psi_n(x)$ is

$$\langle p \rangle = \int_0^a \left[\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right] \left(-i\hbar \frac{d}{dx} \right) \left[\sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \right] dx$$

- Note that the average momentum of a particle in a box is zero.

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- Calculating the variance σ_p^2 of the momentum of a particle in a box.

$$\begin{aligned} \langle p^2 \rangle &= \int \psi_n^* \hat{P}_x^2 \psi_n(x) dx \\ &= \frac{n^2 \pi^2 \hbar^2}{a^2} \end{aligned}$$

- It follows that $\sigma_p = n\pi\hbar/a$.

- **Root-mean-square momentum:** The square root of $\langle p^2 \rangle$.
- “Because the variance σ^2 , and hence the standard deviation σ , is a measure of the spread of a distribution about its mean value, we can interpret σ as a measure of the uncertainty involved in any measurement” (McQuarrie & Simon, 1997, p. 89).
 - For the simple situation of a particle in a box, we can calculate *exact* uncertainties in position and momentum σ_x, σ_p .
 - We can see from these exact formulae that σ_x is directly proportional to the length a of the box, and σ_p is inversely proportional to the length a of the box.
 - This means that as the box gets bigger, it becomes harder to know where the particle is but its momentum becomes more certain, and vice versa as the box gets smaller.
 - From the above, it is clear that σ_x and σ_p have a reciprocal relation.
 - Indeed, taking the product $\sigma_x \sigma_p$ yields the **Heisenberg Uncertainty Principle**

$$\begin{aligned} \sigma_x \sigma_p &= \frac{\hbar}{2} \sqrt{\frac{\pi^2 n^2}{3} - 2} \\ &> \frac{\hbar}{2} \end{aligned}$$

- **Free particle:** A particle that is allowed to range over the entire x -axis.
 - “A free particle has a definite momentum, but its position is completely indefinite” (McQuarrie & Simon, 1997, p. 90).
- The Uncertainty Principle also says that the minimum product of the two uncertainties is on the order of Planck’s constant.
- The particle in a three-dimensional box:
 - If the box (a rectangular parallelepiped) has sides of length a, b, c , then the Schrödinger equation for this case is

$$-\frac{\hbar^2}{2m} \left(\frac{\partial^2 \psi}{\partial x^2} + \frac{\partial^2 \psi}{\partial y^2} + \frac{\partial^2 \psi}{\partial z^2} \right) = E\psi(x, y, z)$$

where $0 \leq x \leq a$, $0 \leq y \leq b$, and $0 \leq z \leq c$.

- An alternate form is

$$-\frac{\hbar^2}{2m} \nabla^2 \psi = E\psi$$

- Boundary conditions:

- $\psi(0, y, z) = \psi(a, y, z) = 0$ for all y, z .
 - $\psi(x, 0, z) = \psi(x, b, z) = 0$ for all x, z .
 - $\psi(x, y, 0) = \psi(x, y, c) = 0$ for all x, y .
- Invoke the method of separation of variables, i.e., suppose

$$\psi(x, y, z) = X(x)Y(y)Z(z)$$

- Then

$$-\frac{\hbar^2}{2m} \frac{1}{X(x)} \frac{d^2 X}{dx^2} - \frac{\hbar^2}{2m} \frac{1}{Y(y)} \frac{d^2 Y}{dy^2} - \frac{\hbar^2}{2m} \frac{1}{Z(z)} \frac{d^2 Z}{dz^2} = E$$

- It follows since each of the three terms contains only one of the variables and hence each of the terms can be varied independently that each term must equal a constant. The sum of the three constants will be E .
- But dividing the above equations into three smaller equations gives us cases entirely analogous to the one-dimensional particle in a box, meaning that

$$X(x) = A_x \sin \frac{n_x \pi x}{a} \quad Y(y) = A_y \sin \frac{n_y \pi y}{b} \quad Z(z) = A_z \sin \frac{n_z \pi z}{c}$$

for $n = 1, 2, 3, \dots$

- Therefore, the solution is

$$\psi(x, y, z) = A_x A_y A_z \sin \frac{n_x \pi x}{a} \sin \frac{n_y \pi y}{b} \sin \frac{n_z \pi z}{c}$$

- The normalization constant then turns out to be

$$1 = \int_0^a \int_0^b \int_0^c \psi^*(x, y, z) \psi(x, y, z) dx dy dz$$

$$A_x A_y A_z = \sqrt{\frac{8}{abc}}$$

- We can now also obtain the following formula for the energies by plugging the full solution back into the original Schrödinger equation.

$$E_{n_x n_y n_z} = \frac{\hbar^2}{8m} \left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2} \right)$$

- McQuarrie and Simon (1997) does calculations to show that $\langle x \rangle = (a/2, b/2, c/2)$ and $\langle p \rangle = 0$.
- Note that we have the following 3D operators:

- Position operator:

$$\hat{\mathbf{R}} = \hat{X}\mathbf{i} + \hat{Y}\mathbf{j} + \hat{Z}\mathbf{k}$$

- Momentum operator:

$$\hat{\mathbf{P}} = -i\hbar \left(\mathbf{i} \frac{\partial}{\partial x} + \mathbf{j} \frac{\partial}{\partial y} + \mathbf{k} \frac{\partial}{\partial z} \right)$$

- Consider the special case where $a = b = c$. Then only one set of values n_x, n_y, n_z corresponds to the lowest energy level, but *three degenerate ones* correspond to the second energy level (211, 121, 112).

- Note that the degeneracy is introduced by the symmetry of the box and is lifted when the box becomes no longer symmetric.

- **Laplacian operator:** The operator ∇^2 .
- **Separable (operator):** An operator that is the sum of multiple variably independent terms.