

Lecture 3

**The Schrödinger equation
Quantum Mechanical Operator**

The Schrödinger equation

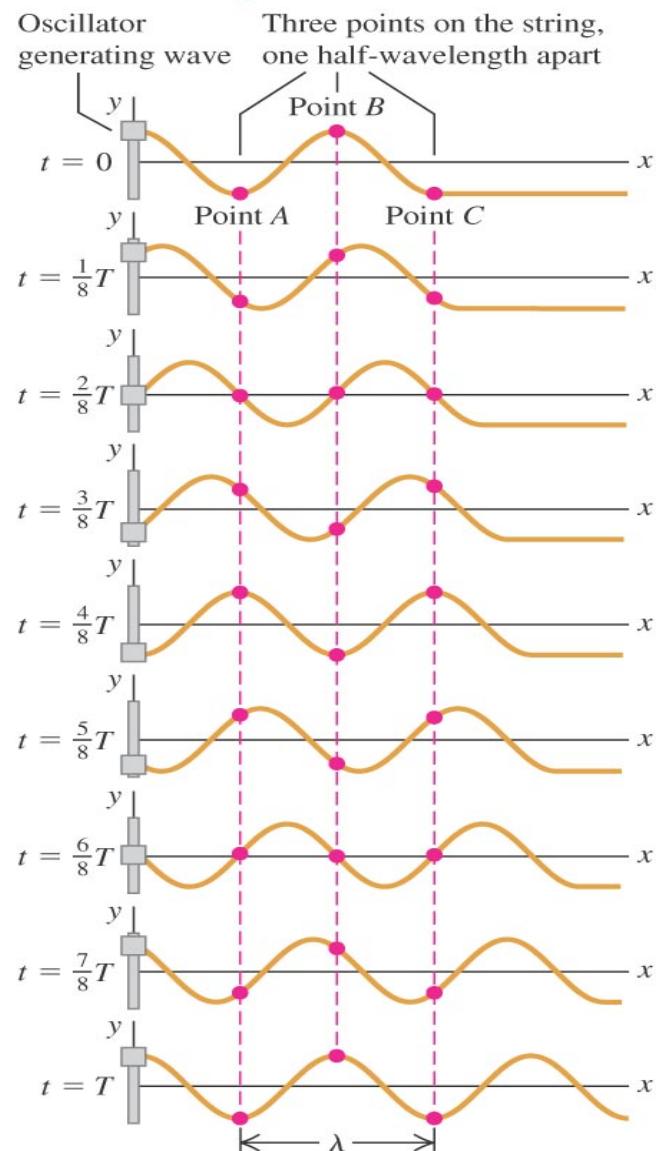
- We introduce **the Schrödinger equation** as the equation of motion of quantum mechanical system.
- We cannot derive it; we postulate it. Its correctness is confirmed by its successful quantitative explanations of all known experimental observations.*

*Some restrictions apply: There are observable effects due to the special theory of relativity such as the spin-orbit coupling, intersystem crossing, and other scalar relativistic effects. These effects can be substantial in heavy elements. There are also observable quantum electrodynamics effects, which cannot be described by the Schrödinger equation, either. They are small.

Mathematical description of a wave

- The *wave function*, $y(x,t)$, gives a mathematical description of a wave. In this function, y is the displacement of a particle at time t and position x .
 - The wave function for a sinusoidal wave moving in the $+x$ -direction is $y(x,t) = A\cos(kx - \omega t)$, where $k = 2\pi/\lambda$ is called the *wave number*.
 - For transverse waves, y might represent the height of the wave at location x .
 - For longitudinal waves, y might represent the pressure at location x .

The string is shown at time intervals of $\frac{1}{8}$ period for a total of one period T .



Derivatives of y : wave equation

- Starting with $y(x, t) = A \cos(kx - \omega t)$, take *partial derivative* with respect to time to get y component of velocity:

$$v_y(x, t) = \frac{\partial y(x, t)}{\partial t} = \omega A \sin(kx - \omega t)$$

- Likewise, take another partial derivative to get y component of acceleration:

$$a_y(x, t) = \frac{\partial^2 y(x, t)}{\partial t^2} = -\omega^2 A \cos(kx - \omega t) = -\omega^2 y(x, t)$$

- We can also take partial derivatives with respect to x (instead of t) to get:

$$\frac{\partial^2 y(x, t)}{\partial x^2} = -k^2 A \cos(kx - \omega t) = -k^2 y(x, t)$$

- If we take the ratio of these two equations, we have:

$$\frac{\partial^2 y(x, t) / \partial t^2}{\partial^2 y(x, t) / \partial x^2} = \frac{\omega^2}{k^2} = v^2$$

- Rearranging gives the wave equation:

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

The Wave Equation

- We saw that the solution to this equation (as can be seen by direct substitution) is $y(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$ where A and B are two constants determined by initial conditions. This solution works as long as $v = \lambda f = \omega/k$.

- In the previous lecture, we introduced de Broglie's idea that matter can also be thought of as wave-like in nature, with energy and momentum given by

$$\checkmark E = hf = \hbar\omega; \quad p = \frac{h}{\lambda} = \hbar k$$

- However, for this case we cannot have such a simple relation as $v = \lambda f = \omega/k$. Writing the total energy of a free particle ($U = 0$), we would have $E = K = p^2/2m$, so

$$\hbar\omega = \frac{\hbar^2 k^2}{2m} \quad (\text{equation 1})$$

- If matter behaves like a wave, we ought to be able to come up with a wave equation for matter, but it has to obey the above relation between ω and k (for the case of a free particle).

The Wave Equation

- Let us look for a wave equation (containing derivatives with respect to x and t) whose solution is

$$\Psi(x, t) = A \cos(kx - \omega t) + B \sin(kx - \omega t)$$

that obeys equation 1: $\hbar\omega = \frac{\hbar^2 k^2}{2m}$

- A second derivative with respect to x brings out a $-k^2$, and a single derivative with respect to t brings out an ω :

$$\frac{\partial^2 \Psi(x, t)}{\partial x^2} = -k^2 [A \cos(kx - \omega t) + B \sin(kx - \omega t)]$$

$$\frac{\partial \Psi(x, t)}{\partial t} = \omega [A \sin(kx - \omega t) - B \cos(kx - \omega t)]$$

- If we multiply the spatial derivative term by $-\frac{\hbar^2}{2m}$ that will give the left side of equation 1.
- We can almost get the right side of equation 1 by multiplying by \hbar , but the time derivative term is a little tricky because the first term has become a sine function while the second term became a negative cosine. We need a factor C such that $A \cos(kx - \omega t) + B \sin(kx - \omega t) = C [A \sin(kx - \omega t) - B \cos(kx - \omega t)]$

The Schrödinger Equation

- Clearly $A = -BC$, and $B = CA$ will do the trick. Thus, $A = -C^2A$, which means $C^2 = -1$, so $C = \sqrt{-1} = i$.
- The final wave equation that seems to work is
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x, t)}{\partial x^2} = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$
.
- This is the one-dimensional wave equation for a free particle, and is a special case of the Schrödinger equation, first developed by Erwin Schrödinger in 1926.
- Since $C = i$, $B = iA$, so we can write the wave function (solution) as

$$\Psi(x, t) = A[\cos(kx - \omega t) + i \sin(kx - \omega t)]$$

which is a complex function with real part $\text{Re}[\Psi(x, t)] = A \cos(kx - \omega t)$, and imaginary part $\text{Im}[\Psi(x, t)] = A \sin(kx - \omega t)$. This represents a particle moving to the right if k is positive, and to the left if k is negative.

- Using Euler's formula $e^{\pm i\theta} = \cos \theta \pm i \sin \theta$, the wave function can be written more compactly as

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

The Schrödinger equation in 1-D

- We found that the one-dimensional Schrödinger equation for a free particle of mass m is

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

- How do we interpret the complex solution $\Psi(x,t) = Ae^{i(kx-\omega t)}$? This represents a distribution of “something” in space and time. Any real quantity, however, must have a real solution. Recall that we interpreted the interference intensity pattern as representing the square of the electric field, and individual photons land on a screen with a probability given by the intensity pattern (more land where the intensity is high, fewer land where it is low). Likewise, the quantity

$$|\Psi(x,t)|^2 = \Psi(x,t)\Psi^*(x,t) = Ae^{i(kx-\omega t)}A^*e^{-i(kx-\omega t)}$$

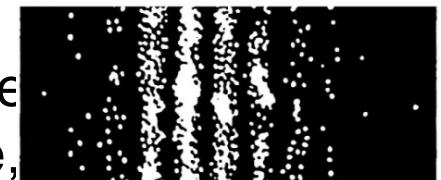
is the (real) probability in space and time where the particle will be found, where the * represents the complex conjugate found by replacing i with $-i$.

- The square of the abs. value of the wave function, $|\Psi(x,t)|^2$, is the probability distribution function. It tells us the probability of finding the particle near position x at time t .

After 21 photons reach the screen



After 1000 photons reach the screen



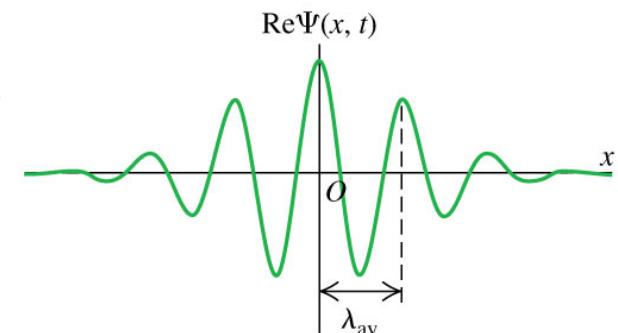
After 10,000 photons reach the screen



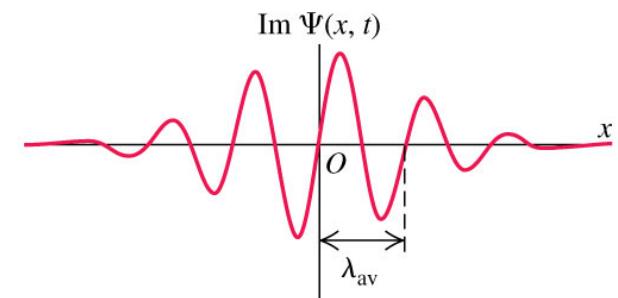
The Schrödinger equation in 1-D: Wave packets

- If $\Psi(x, t) = A e^{i(kx - \omega t)}$ is a solution to the Schrödinger equation, any superposition of such waves is also a solution. This would be written:
$$\Psi(x, t) = \int_{-\infty}^{\infty} A(k) e^{i(kx - \omega t)} dk$$
- A free-particle wave packet localized in space (see Figure at right) is a superposition of states of definite momentum and energy.
- The function itself is “wavy,” but the probability distribution function is not.
- The more localized in space a wave packet is, the greater the range of momenta and energies it must include, in accordance with the Heisenberg uncertainty principle.
- The Schrödinger equation discussed so far is only for a free particle (in a region where potential energy $U(x) = 0$). We will now add non-zero $U(x)$.

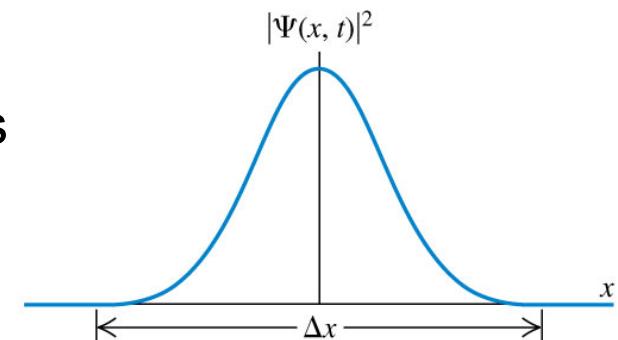
(a) Real part of the wave function at time t



(b) Imaginary part of the wave function at time t



(c) Probability distribution function at time t



The Schrödinger equation in 1-D

- If a particle of mass m moves in the presence of a potential energy function $U(x)$, the one-dimensional Schrödinger equation for the particle is
$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} + U(x) \Psi(x,t) = i\hbar \frac{\partial \Psi(x,t)}{\partial t} \quad (\text{general 1D Schrödinger equation})$$
- This equation can be thought of as an expression of conservation of energy, $K + U = E$. Inserting $\Psi(x,t) = A e^{i(kx - \omega t)}$, the first term is K times $\Psi(x,t)$

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi(x,t)}{\partial x^2} = -\frac{\hbar^2}{2m} (ik)^2 \Psi(x,t) = \frac{\hbar^2 k^2}{2m} \Psi(x,t) = \frac{p^2}{2m} \Psi(x,t)$$

- Likewise, the term on the RHS is E times $\Psi(x,t)$.

$$i\hbar \frac{\partial \Psi(x,t)}{\partial t} = i\hbar(-i\omega) \Psi(x,t) = \hbar\omega \Psi(x,t)$$

- For a particle in a region of space with non-zero $U(x)$, we have to add the term $U(x)\Psi(x, t)$ on the left to include the potential energy.
- Let's write the wave function in *separable form*, where the lower-case $\psi(x)$ is the time-independent wave function.

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

- Further, we can write $\omega = E / \hbar$, so that $\Psi(x,t) = \psi(x) e^{-iEt/\hbar}$.

The Schrödinger equation

- The correct equation of motion that works for microscopic particles was proposed by Erwin Schrödinger.

$$\hat{H}\Psi = E\Psi$$

Hamiltonian

Wave function

Energy



The Schrödinger equation

Erwin Schrödinger

Hamilton's representation of classical mechanics

Newton's equation of motion = the conservation
of energy (kinetic + potential energies = constant)

$$H = E$$

Hamiltonian Energy

Classical

$$H = \frac{p^2}{2m} + V(x)$$

Kinetic energy

Potential energy

Hamilton's representation of classical mechanics

$$H = E \rightarrow \frac{\partial H}{\partial t} = 0$$

$$H = \frac{p^2}{2m} + V(x)$$

$$\rightarrow 0 = \frac{\partial H}{\partial t} = \frac{\partial}{\partial t} \frac{p^2}{2m} + \frac{\partial V(x)}{\partial t} = \frac{2p}{2m} \frac{\partial p}{\partial t} + \frac{\partial x}{\partial t} \frac{\partial V(x)}{\partial x} = vma + v(-F)$$

$$v \rightarrow F = ma \quad ma \quad -F$$

The Schrödinger equation

- In quantum mechanics, energy should be conserved, just as in classical mechanics.
- Schrödinger used the Hamilton's equation as the basis of quantum mechanics.

Quantum

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

Classical

$$H = E; H = \frac{p^2}{2m} + V(x)$$

Hamilton's representation of classical mechanics

- In classical mechanics, H is a **function** of p , m , and x ; p and x are functions of time.
- Once we know the mass (m), position (x), and velocity ($p = mv$) of a **particle**, we can know the exact trajectory (positions as a function of time) of the particle from the classical mechanics.

$$H = E; H = \frac{p^2}{2m} + V(x)$$

The Schrödinger equation

- However, the concept of trajectory is strictly for particles only. Schrödinger needed to modify the equation to account for the wave-particle duality.
 - Introduction of a **wave function**.

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

Wave function

The Schrödinger equation

- The equation must also give energies that are quantized
 - The **operator** form of equation.

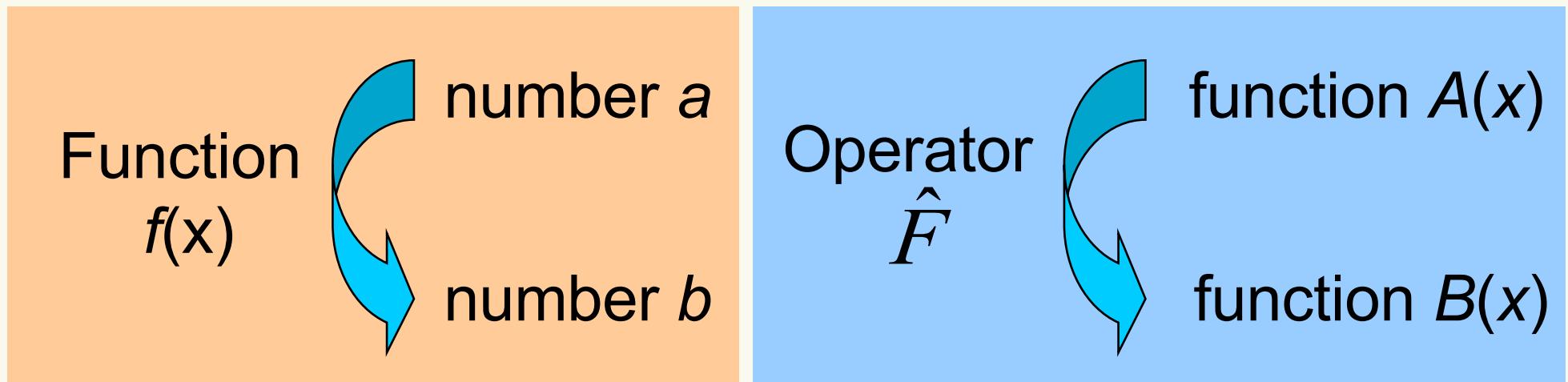
H is now an **operator**
(it has a “^” hat sign)

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

Kinetic energy **operator**

What is an operator?

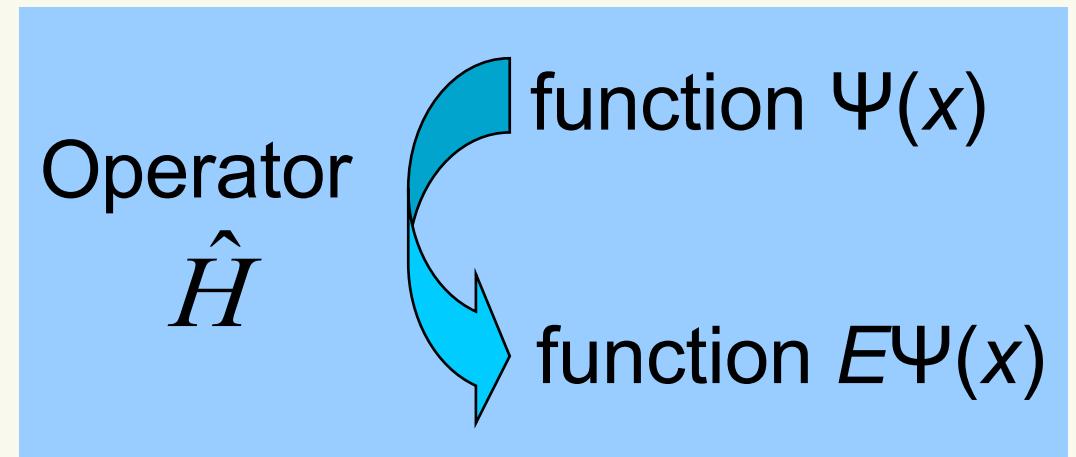
- An operator carries out a mathematical operation (multiplication, differentiation, integrations, etc.) on a given function.



The Schrödinger equation

- Generally, when function A is acted on by an operator, a different function (B) results.
- The Schrödinger equation says that the input and output functions should be the same (Ψ), apart from a constant factor (E).

$$\hat{H}\Psi = E\Psi$$



Eigenvalues and Eigenfunctions

- In general, operator Ω (omega) and a function ψ (psi) satisfy the equation of the form:

$$\hat{\Omega} \psi = \omega \psi$$

There are infinitely many eigenfunctions and eigenvalues

where ω is some constant factor, we call ω an **eigenvalue** of the operator Ω and ψ an **eigenfunction** of Ω . The equation of this form is called **eigenvalue equation**.

The Schrödinger equation

- A wave function *associated with a well-defined energy* is an **eigenfunction** of the H operator with the **eigenvalue** being the energy.
- Not any arbitrary value of energy can be an eigenvalue of the H operator.
- This eigenvalue form of the Schrödinger equation makes the energies quantized.*

*Strictly speaking, it is the boundary condition together with the eigenvalue form of the equation that causes the energies to be quantized. We will learn about the importance of the boundary condition in a partial differential equation shortly.

The Hamiltonian operator

- \hat{H} is called the Hamiltonian operator.
- It is an operator for energy.

$$\hat{H} = \underbrace{-\frac{\hbar^2}{2m} \frac{d^2}{dx^2}}_{\text{Kinetic energy operator}} + \underbrace{\hat{V}(x)}_{\text{Potential energy operator}}$$

The Hamiltonian operator

- The kinetic energy operator is the operator for kinetic energy:

$$\frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$\hbar = h / 2\pi \text{ (\hbar is called the } h \text{ bar)}$$

- How can this classical to quantum translation be justified?

The Hamiltonian operator

- Again, this form is postulated, not derived. We can try to imagine the thought process of Schrödinger who came up with this translation.
- First, we see that postulating

$$\frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

is the same as postulating

$$p \rightarrow -i\hbar \frac{d}{dx}; i = \sqrt{-1}$$

The Hamiltonian operator

$$p \rightarrow -i\hbar \frac{d}{dx}$$

$$p^2 \rightarrow -i\hbar \frac{d}{dx} \left(-i\hbar \frac{d}{dx} \right) = (-i\hbar)^2 \frac{d^2}{dx^2} = -\hbar^2 \frac{d^2}{dx^2}$$

$$\frac{p^2}{2m} \rightarrow -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}$$

$$i^2 = (\sqrt{-1})^2 = -1$$

$$\frac{d(AB)}{dx} = \frac{dA}{dx}B + \frac{dB}{dx}A$$

The momentum operator

- Let us call

$$-i\hbar \frac{d}{dx}$$

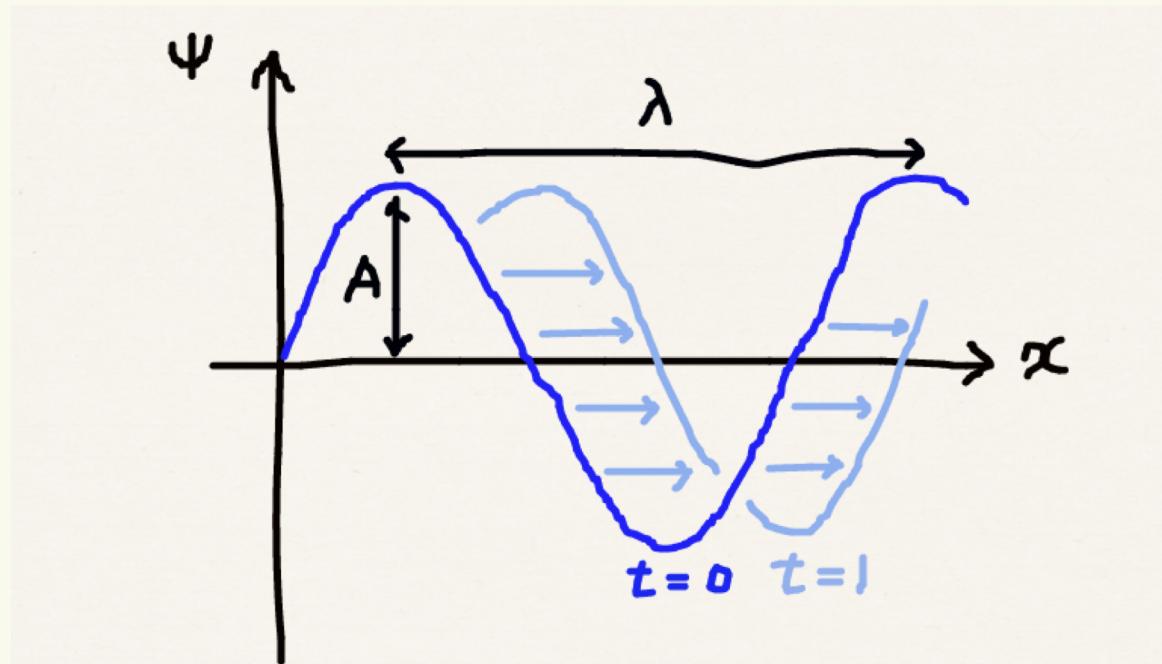
the momentum operator and try to justify it.

- We will apply this to a “simple wave” to see that it is indeed an operator for a momentum.

The simple wave

- A function describing a simple sinusoidal wave with wave length λ (lambda) and frequency ν (nu):

$$\Psi(x,t) = A \cos\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right) \quad \Psi(x,t) = A \sin\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)$$



The simple wave

- Euler' s relation

$$e^{i\theta} = \cos \theta + i \sin \theta$$

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \dots$$

$$\cos x = 1 - \frac{x^2}{2!} + \frac{x^4}{4!} - \dots; \sin x = x - \frac{x^3}{3!} + \frac{x^5}{5!} - \dots$$

- Let us use this to represent the simple wave

$$e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)}$$

The momentum operator

- We act the momentum operator on the simple wave

$$p \rightarrow -i\hbar \frac{d}{dx}$$

$$\Psi = e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)}$$

$$\begin{aligned}-i\hbar \frac{d}{dx} \Psi &= -i\hbar \frac{d}{dx} e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)} = -i\hbar \left(i \frac{2\pi}{\lambda}\right) e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)} \\ &= -i^2 \frac{\hbar}{2\pi} \frac{2\pi}{\lambda} \Psi = \frac{\hbar}{\lambda} \Psi\end{aligned}$$

The momentum operator

- The simple wave is an **eigenfunction** of the momentum operator with the **eigenvalue** h / λ .

$$-i\hbar \frac{d}{dx} \Psi = \frac{h}{\lambda} \Psi$$

- According to **de Broglie relation**:

$$p = \frac{h}{\lambda}$$

- The momentum operator makes sense.

Time-dependent Schrödinger equation

- We have seen the effect of an operator that differentiates with respect to x (position).
- What if we differentiate with respect to t (time)?

$$\begin{aligned} i\hbar \frac{d}{dt} \Psi &= i\hbar \frac{d}{dt} e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)} = i\hbar(-i2\pi\nu)e^{i\left(\frac{2\pi}{\lambda}x - 2\pi\nu t\right)} \\ &= -i^2 \frac{\hbar}{2\pi} 2\pi\nu \Psi = \hbar\nu\Psi \end{aligned}$$

Time-dependent Schrödinger equation

- To reiterate the result:

$$i\hbar \frac{d}{dt} \Psi = h\nu \Psi$$

- A sinusoidal wave is an **eigenfunction** of an operator $i\hbar \frac{d}{dt}$ with an **eigenvalue** of $h\nu$.
- According to Planck, $h\nu$ is the energy of an oscillator with frequency ν .

Time-dependent Schrödinger equation

- We have found an operator for energy:

$$E \rightarrow i\hbar \frac{d}{dt}$$

- Substituting this into the **time-independent** Schrödinger equation ($\hat{H}\Psi = E\Psi$), we obtain **time-dependent** Schrödinger equation

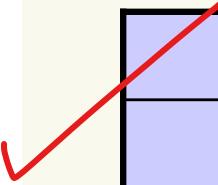
$$\hat{H}\Psi = i\hbar \frac{d\Psi}{dt}$$

Summary

- We have introduced the Schrödinger equation – the equation of motion of quantum mechanics and “the whole of chemistry.”*
- The time-independent Schrödinger equation parallels Hamilton’s equation in classical mechanics and physically represents conservation of energy.
- It incorporates the wave-particle duality and quantization of energy.

*In the words of Paul Dirac.

Summary



	Classical	Quantum
Position	x	\hat{x}
Momentum	$p = mv$	$-i\hbar(d / dx)$
Potential energy	V	\hat{V}
Energy	E	E or $i\hbar(d / dt)$
Equation	$H = E$	$\hat{H}\Psi = E\Psi$ $\hat{H}\Psi = i\hbar(d / dt)\Psi$
Wave-particle duality	No. Particle only	Yes via the wave function
Quantization	Continuous and nearly arbitrary	Eigenvalues and quantized