# 8/28/2024

- Postulates of quantum mechanics
  - States and wavefunctions
  - Observables and representations
  - The outcome of measurements
    - Eigenfunction expansions, including Fourier series
    - Collapse of wavefunctions and Schrödinger's cat
  - The Born interpretation: probabilities of particle positions
  - The Schrödinger equation
    - The Hamiltonian operator
    - Time-independent form by separation of variables
    - Time dependence of the wavefunction

# Postulates

- This module is intended to help you achieve the following learning objectives:
  - Recall and explain the postulates of quantum mechanics
- At the end of this module, you should be able to
  - answer the following questions:
    - What does a wavefunction describe?
    - What the the commutators for position and momentum operators?
    - How do you evaluate an expectation value if the wavefunction is not an eigenfunction of an operator?
    - What happens if you perform a measurement on a superposition state?
    - What is the probability of finding a particle in a particular region?
    - What is the time-independent Schrödinger equation?

# About the Postulates

- Assumptions that are the basis of quantum mechanics
- Are *not* intuitive
- Not provable
- Results consistent with observations

# 1. States and wavefunctions

- The state of a system is fully described by a function $\Psi(r_1, r_2, \ldots, t)$, known as the wavefunction
  - $r_n$ is the position of particle $n$
    - particles can include electrons and nuclei
  - $t$ is time, which is often not considered
- Over semester, we will study progressively more complex $\Psi$ with more and more particles and dimensions

# 2. Observables

- Observables are *represented* by Hermitian operators chosen to satisfy the the commutation relations $[q, p_{q'}] = i\hbar\delta_{qq'}$, $[q, q'] = 0$, $[p_q, p_{q'}] = 0$.
  - $q$ and $q'$ are coordinates like $x$, $y$, and $z$. They may be the same or different.
  - $p_q$ is the momentum in the direction of $q$
  - $i = \sqrt{-1}$
  - $\hbar = \dfrac{h}{2\pi}$, where $h = 6.62607015 \times 10^{-34} \ \mathrm{J.Hz^{-1}}$ is Plank's constant
  - $\delta_{qq'}$ is a Kronecker delta function. It is one when $q = q'$ and zero if $q \neq q'$.
- *Any* set of operators that satisfy this postulate may be chosen
- Many QM manipulations can actually be performed without representations

# Representations

- Set of operators that *represent* observables
- The most popular are
  - Position representation
    - $x \rightarrow x \times$
    - $p_x \rightarrow \dfrac{\hbar}{i} \dfrac{\partial}{\partial x}$
  - Momentum representation
    - $x \rightarrow -\dfrac{\hbar}{i} \dfrac{\partial}{\partial p_x}$
    - $p_x \rightarrow p_x \times$
  - More generally, $x$ may be replaced by $q$, which is $x$, $y$, or $z$.

# Representations and Postulate 2

Does the position representation satisfy $[q, p_{q'}] = i\hbar\delta_{qq'}$? Here is how to show this.

$$\left[q, \frac{\hbar}{i}\frac{\partial}{\partial q'}\right]f = q\frac{\hbar}{i}\frac{\partial f}{\partial q'} - \frac{\hbar}{i}\frac{\partial}{\partial q'}(qf)$$

$$= \frac{\hbar}{i}\left[q\frac{\partial f}{\partial q'} - \frac{\partial q}{\partial q'}f - q\frac{\partial f}{\partial q'}\right]$$

$$= -\frac{\hbar}{i}\frac{\partial q}{\partial q'}f = i\hbar\delta_{qq'}f$$

- Position representation
  - $x \rightarrow x$
  - $p_x \rightarrow \dfrac{\hbar}{i}\dfrac{\partial}{\partial x}$
- Momentum representation
  - $x \rightarrow -\dfrac{\hbar}{i}\dfrac{\partial}{\partial p_x}$
  - $p_x \rightarrow p_x$

# Representations and Postulate 2

Does the momentum representation satisfy
$[q, p_{q'}] = i\hbar\delta_{qq'}$? Try it.

$$\left[-\frac{\hbar}{i}\frac{\partial}{\partial p_q}, p_{q'}\right]f$$

$$= -\frac{\hbar}{i}\left[\frac{\partial}{\partial p_q}(p_{q'}f) - p_{q'}\frac{\partial f}{\partial p_q}\right]$$

$$= -\frac{\hbar}{i}\frac{\partial p_{q'}}{\partial p_q}f = i\hbar\delta_{qq'}f$$

- Position representation
  - $x \to x$
  - $p_x \to \frac{\hbar}{i}\frac{\partial}{\partial x}$
- Momentum representation
  - $x \to -\frac{\hbar}{i}\frac{\partial}{\partial p_x}$
  - $p_x \to p_x$

# 3. The outcome of measurements

The mean value of the observable in a series of measurements is equal to the expectation value of the corresponding operator,

$$\langle A \rangle = \frac{\left\langle \Psi \left| \hat{\mathbf{A}} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle}$$

- This is like the expectation value of flipping a coin or rolling dice
- $\langle \Psi | \Psi \rangle$ is a normalizing constant. If $\Psi$ is normalized (as we will assume), then $\langle \Psi | \Psi \rangle = 1$ can be omitted from the expectation value.

# What if $\Psi$ is not an eigenfunction of $\hat{A}$?

- If $\hat{\mathbf{A}}\Psi = a\Psi$, then $\langle A \rangle = \left\langle \Psi \left| \hat{\mathbf{A}} \right| \Psi \right\rangle = a$.

- Otherwise, we can expand $\Psi$ in terms of basis functions - building blocks for more complex functions

# Eigenfunction Expansions

- Any function may be expressed as a linear combination of *all* the eigenfunctions of an operator, $g = \sum_n c_n f_n.$

  - $c_n$ are coefficients

  - $f_n$ are eigenfunctions. They are basis functions for $g$.

# Example Eigenfunctions

- Any function may be expressed as a linear combination of *all* the eigenfunctions of an operator, $g = \sum\limits_{n} c_n f_n$.

- Consider the operator $\hat{\mathbf{A}} = \dfrac{d^2}{dx^2}$. What are the eigenfunctions? Hint: we talked about one in the last class period.

  - $\sin(ax)$, where $a$ is a positive integer. The eigenvalue is $-a^2$.

  - $\cos(bx)$, where $b$ is a positive integer. The eigenvalue is $-b^2$.

  - $c$, a number. The eigenvalue is 0.

# **Fourier Series**

- An expansion of a periodic function in terms of sines and cosines
- To the right: the first four partial sums of the Fourier series for a square wave. As more terms are added, the partial sums converge to the square wave.
- For more details, examples, and expressions for coefficients, see Wolfram MathWorld.
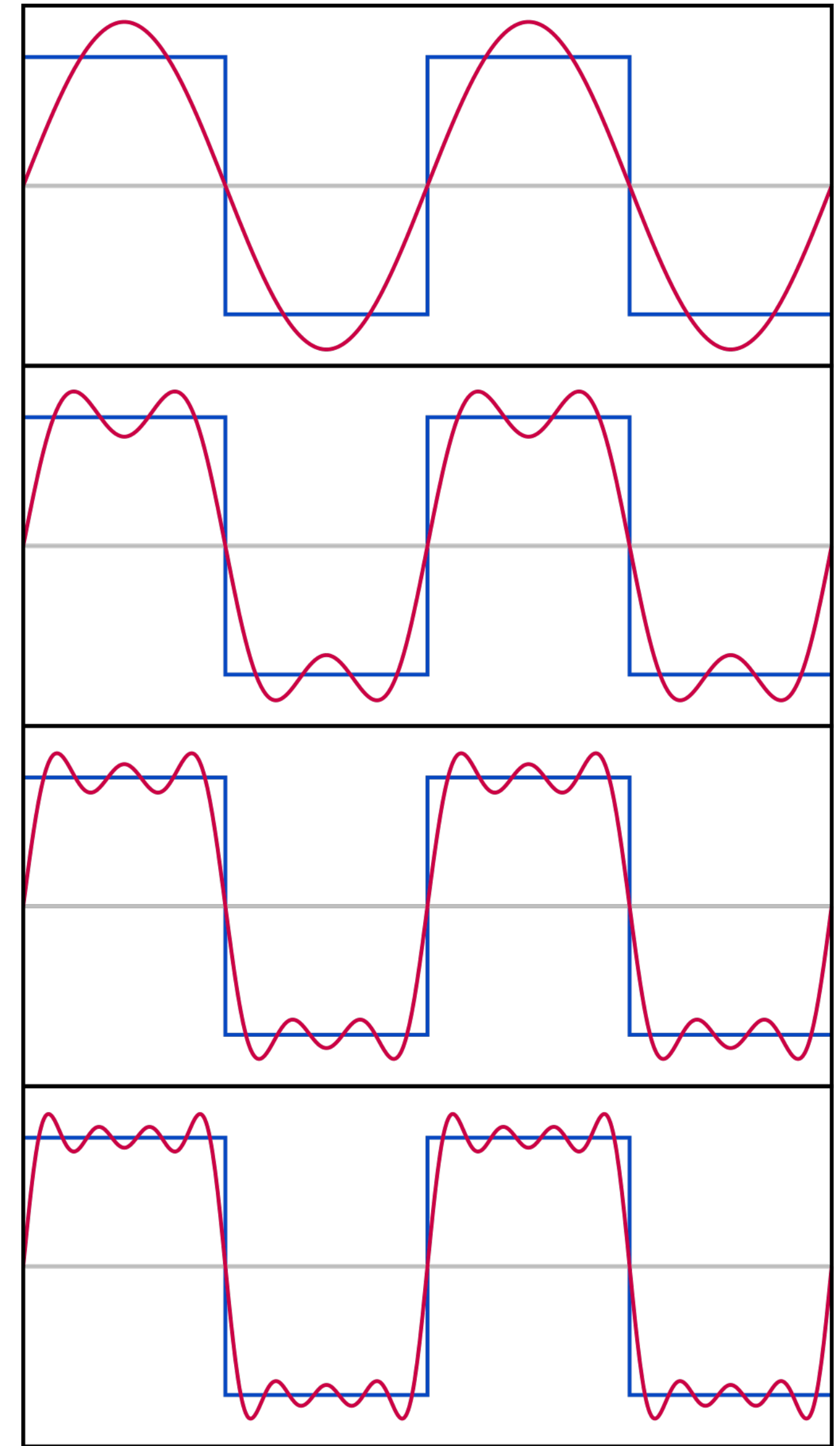
# Mean values for linear combinations

- Given $\Psi = \sum\limits_{m} c_m \Psi_m$, the probability of measuring a particular eigenvalue $\omega_n$

  is proportional to $|c_m|^2$.
  - $c_m$ is the coefficient
  - $\Psi_m$ are eigenfunctions of $\hat{\mathbf{A}}$

- $|c_m|^2$ can be thought of as weights in a weighted sum,

$$\langle A \rangle = \int \left( \sum_n c_n \Psi_n \right)^* \hat{\mathbf{A}} \left( \sum_m c_m \Psi_m \right) d\tau = \sum_n \sum_m \int \left( c_n \Psi_n \right)^* \left( a_m c_m \Psi_m \right) d\tau = \sum_m a_m |c_m|^2$$

# Measurement

- Immediately after the *measurement*, the state of the system will be $\Psi_n$
- Unlike in classical mechanics, in QM, measurement alters the system. It makes the system *collapse* onto a state.
- This implies that before measurement, the system described by $\Psi = \sum_m c_m \Psi_m$ is in a *superposition* of states.
- Does this make sense? Schrödinger didn't think so. Yet this *Copenhagen interpretation* of QM remains.

# Schrödinger's Cat
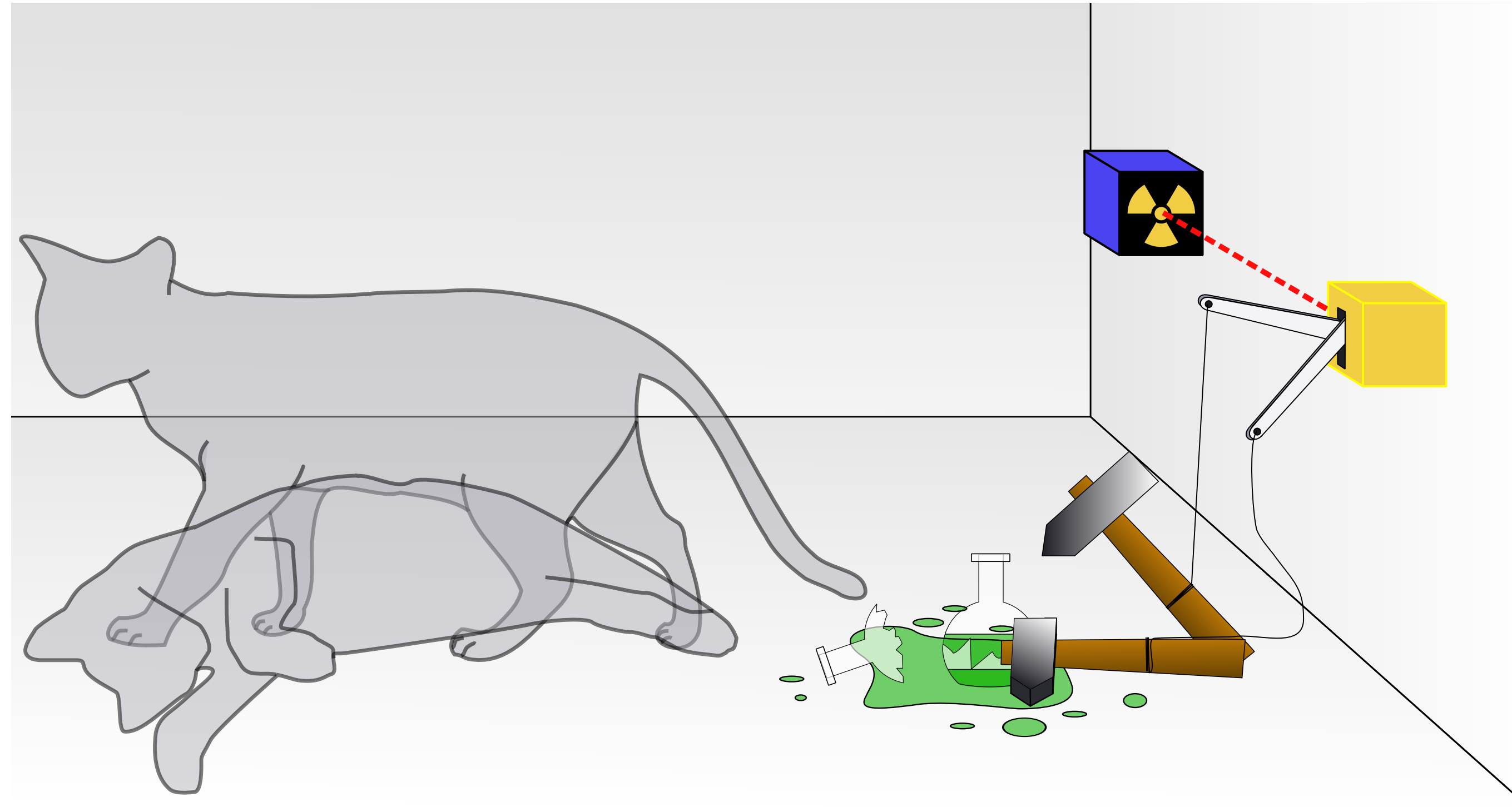


By Dhatfield - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=4279886
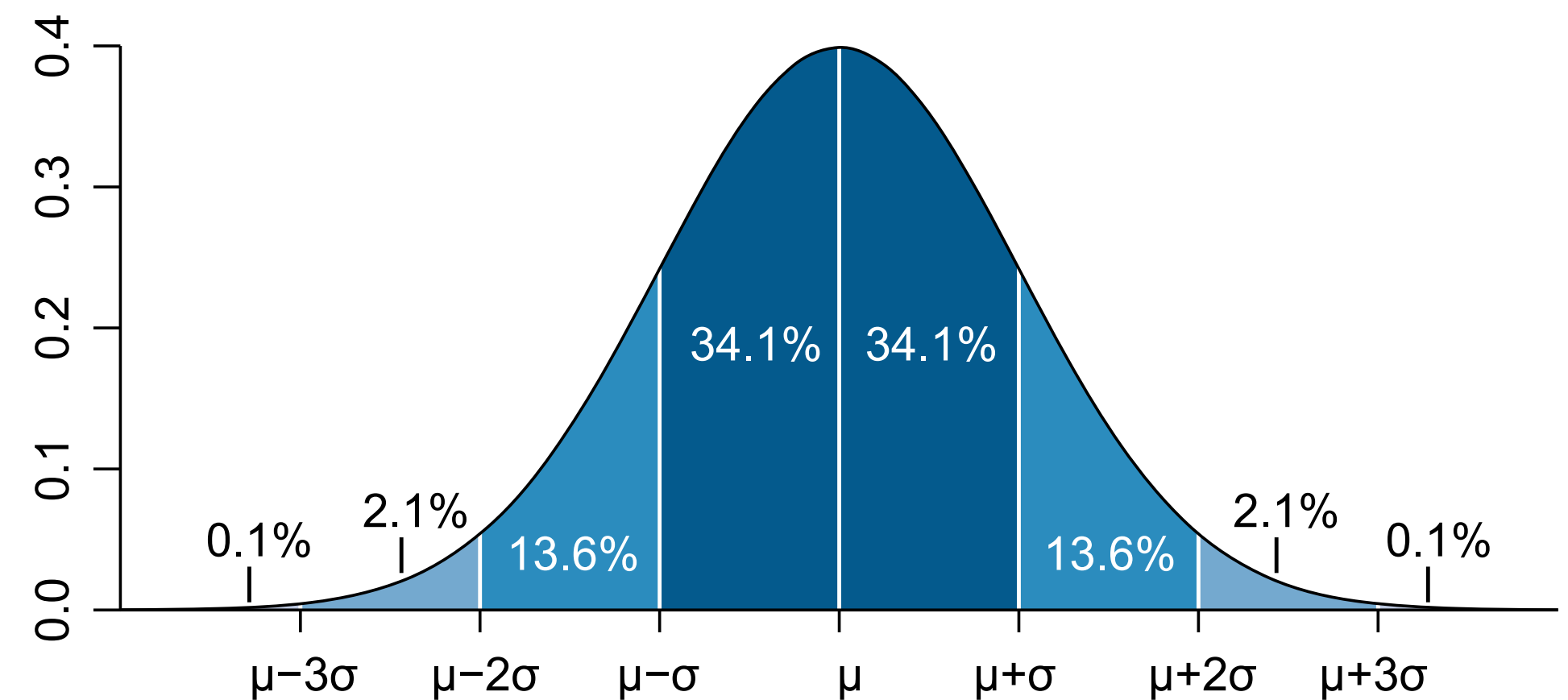
Schrödinger's cat: a cat, a flask of poison, and a radioactive source connected to a Geiger counter are placed in a sealed box. As illustrated, the objects are in a state of superposition: the cat is both alive and dead.

# 4. Probabilities of particle positions

- Born interpretation: the probability that a particle will be found in the volume element $d\tau$ at the point $r$ is proportional to $|\Psi(r)|^2 d\tau$.

- The probability density function is $|\Psi(r)|^2$

- $\displaystyle\int |\Psi|^2 d\tau < \infty$ because the particle must be somewhere

PDF of a normal distribution



By Ainali - Own work, CC BY-SA 3.0, https://commons.wikimedia.org/w/index.php?curid=3141713

$$f(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}^2\right)}$$

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# 5. The equation for the wavefunction

- The wavefunction evolves in time according to the time-dependent

  Schrödinger equation, $i\hbar\dfrac{\partial \Psi}{\partial t} = \hat{\mathbf{H}}\Psi$

  - introduced by Erwin Schrödinger in 1926
- If the potential energy is time-independent, then the equation may be
  simplified to the time-independent Schrödinger equation, $\hat{\mathbf{H}}\Psi = E\Psi$
  - the focus of this class
  - can be derived by separation of variables (will do so shortly)
- $\hat{\mathbf{H}}$ is the Hamiltonian operator, which specifies the total (kinetic + potential)
  energy of the system

# The Hamiltonian operator

- $\hat{\mathbf{H}}$ is the Hamiltonian operator, which specifies the total (kinetic + potential) energy of the system
- The kinetic energy of a particle with mass $m$ and momentum $p$ is

- $T = \dfrac{p^2}{2m}$

- In the position representation, $\hat{\mathbf{T}} = \dfrac{\hbar^2}{2m}\nabla^2$. $\nabla^2 = \dfrac{\partial^2}{\partial x^2} + \dfrac{\partial^2}{\partial y^2} + \dfrac{\partial^2}{\partial z^2}$.

- The potential energy of a particle depends on the system. Over the semester we will consider different potential energy functions

# Time-Independent Schrödinger equation

using separation of variables to derive $\hat{\mathbf{H}}\Psi = E\Psi$

# Separation of Variables, p. 1

- The Schrödinger equation is $\hat{\mathbf{H}}\Psi = i\hbar\dfrac{\partial\Psi}{\partial t}$

- In one dimension, this is $-\dfrac{\hbar}{2m}\dfrac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = i\hbar\dfrac{\partial\Psi}{\partial t}$

- Separation of variables works by assuming that $\Psi(x, t) = \Psi(x)\Theta(t)$, which is true if the potential does not vary with time

- This yields $-\dfrac{\hbar^2}{2m}\Theta\dfrac{\partial^2\Psi}{\partial x^2} + V(x)\Psi\Theta = i\hbar\Psi\dfrac{\partial\Theta}{\partial t}$

# Separation of Variables, p. 2

- Dividing by $\Psi\Theta$ gives, $-\dfrac{\hbar^2}{2m}\dfrac{1}{\Psi}\dfrac{\partial^2\Psi}{\partial x^2} + V(x) = i\hbar\dfrac{1}{\Theta}\dfrac{\partial\Theta}{\partial t}$

  - The lhs is solely a function of $x$ and the rhs is solely a function of $t$; they are separable.
  - When $x$ changes, the rhs does not change. When $t$ changes, the lhs does not change.
  - Both sides are equal to a constant, E.
- As a self-test, write the two eigenfunction equations
  - $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = \hat{\mathbf{H}}\Psi = E\Psi$    Time-independent Schrödinger equation
  - $i\hbar\dfrac{\partial\Theta}{\partial t} = E\Theta$

# Time Dependence

- One of the differential equations is $i\hbar\dfrac{\partial\Theta}{\partial t} = E\Theta$

- What is the solution of this differential equation?
  - $\Theta = e^{-\frac{iE}{\hbar}t}$

- Thus if we have a solution for $\hat{\mathbf{H}}\Psi = E\Psi$, the complete equation is $\Psi(x, t) = \Psi(x)e^{-\frac{iE}{\hbar}t}$.

- Recall the Born interpretation: the probability that a particle will be found in the volume element $d\tau$ at the point $r$ is proportional to $|\Psi(r)|^2 d\tau$. Does the probability of the particle position depend on time?
  - No

# Summary of Postulates

- The state of a system is fully described by a function $\Psi(r_1, r_2, \ldots, t)$, known as the wavefunction

- Observables are *represented* by Hermitian operators chosen to satisfy the the commutation relations $[q, p_{q'}] = i\hbar\delta_{qq'}$, $[q, q'] = 0$, $[p_q, p_{q'}] = 0$

- The mean value of the observable in a series of measurements is equal to the expectation value of the corresponding operator. For an eigenfunction expansion $\Psi = \sum_m c_m \Psi_m$, the probability of measuring a particular eigenvalue $\omega_n$ is proportional to $|c_m|^2$. Measurement makes the system *collapse* onto a state.

- The probability that a particle will be found in the volume element $d\tau$ at the point $r$ is proportional to $|\Psi(r)|^2 d\tau$.

- The wavefunction evolves in time according to $i\hbar\dfrac{\partial\Psi}{\partial t} = \hat{\mathbf{H}}\Psi$. If the potential energy is time-independent, then $\hat{\mathbf{H}}\Psi = E\Psi$

# Review

- What does a wavefunction describe?
- What the the commutators for position and momentum operators?
- How do you evaluate an expectation value if the wavefunction is not an eigenfunction of an operator?
- What happens if you perform a measurement on a superposition state?
- What is the probability of finding a particle in a particular region?
- What is the time-independent Schrödinger equation?