

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
- This lecture is designed to help you achieve the following learning objectives
 - Recall and explain the postulates of quantum mechanics
 - Evaluate expectations for given wave functions

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 $\Psi(r_1, r_2, \dots, t)$, 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 Ψ 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
- $i = \sqrt{-1}$
- $\hbar = \frac{h}{2\pi}$, where $h = 6.62607015 \times 10^{-34} \text{ J} \cdot \text{Hz}^{-1}$ 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
 - $x \rightarrow x \times$
 - $p_x \rightarrow \frac{\hbar}{i} \frac{\partial}{\partial x}$
 - Momentum representation
 - $x \rightarrow -\frac{\hbar}{i} \frac{\partial}{\partial p_x}$
 - $p_x \rightarrow p_x \times$
- 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.

$$\begin{aligned} \left[q, \frac{\hbar}{i} \frac{\partial}{\partial q'} \right] f &= q \frac{\hbar}{i} \frac{\partial f}{\partial q'} - \frac{\hbar}{i} \frac{\partial}{\partial q'} (qf) \\ &= \frac{\hbar}{i} \left[q \frac{\partial f}{\partial q'} - \frac{\partial q}{\partial q'} f - q \frac{\partial f}{\partial q'} \right] \\ &= - \frac{\hbar}{i} \frac{\partial q}{\partial q'} f = i\hbar \delta_{qq'} f \end{aligned}$$

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

Representations and Postulate 2

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

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

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,

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

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

What if Ψ is not an eigenfunction of \hat{A} ?

- If $\hat{A}\Psi = a\Psi$, then $\langle A \rangle = \langle \Psi | \hat{A} | \Psi \rangle = a$.
- Otherwise, we can expand Ψ in terms of basis functions - building blocks for more complex functions

Eigenfunction Expansions

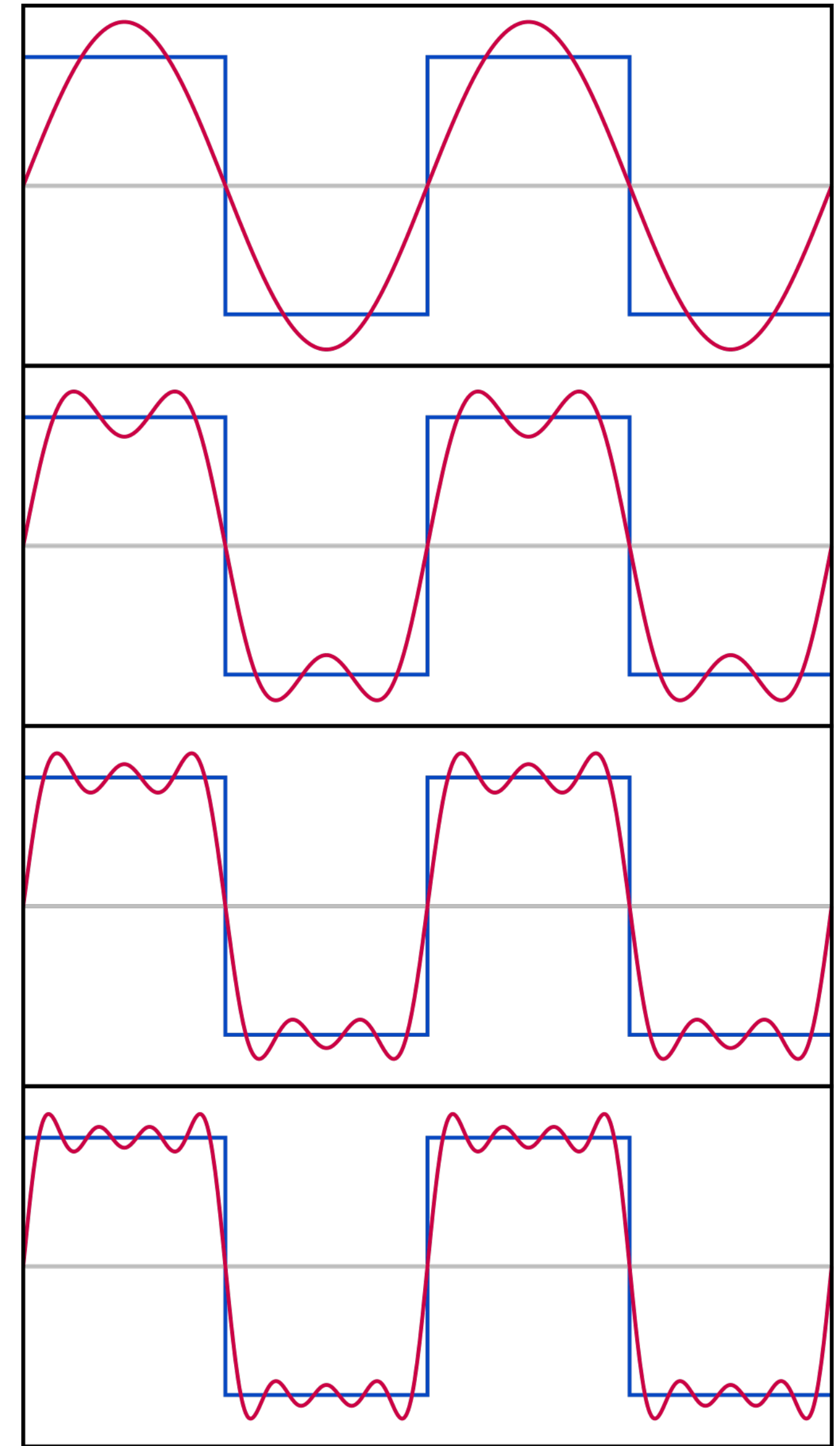
- Any function may be expressed as a linear combination of *all* the eigenfunctions of an operator, $g = \sum_n c_n f_n$.
- c_n are coefficients
- f_n are eigenfunctions. They are basis functions for g .

Example Eigenfunctions

- Any function may be expressed as a linear combination of *all* the eigenfunctions of an operator, $g = \sum_n c_n f_n$.
- Consider the operator $\hat{A} = \frac{d^2}{dx^2}$. What are the eigenfunctions? Hint: we talked about one in the last class period.

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](https://mathworld.wolfram.com/FourierSeries.html).



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Mean values for linear combinations

- Given $\Psi = \sum_m c_m \Psi_m$, the probability of measuring a particular eigenvalue ω_n is proportional to $|c_m|^2$.

- c_m is the coefficient

- Ψ_m are eigenfunctions of \hat{A}

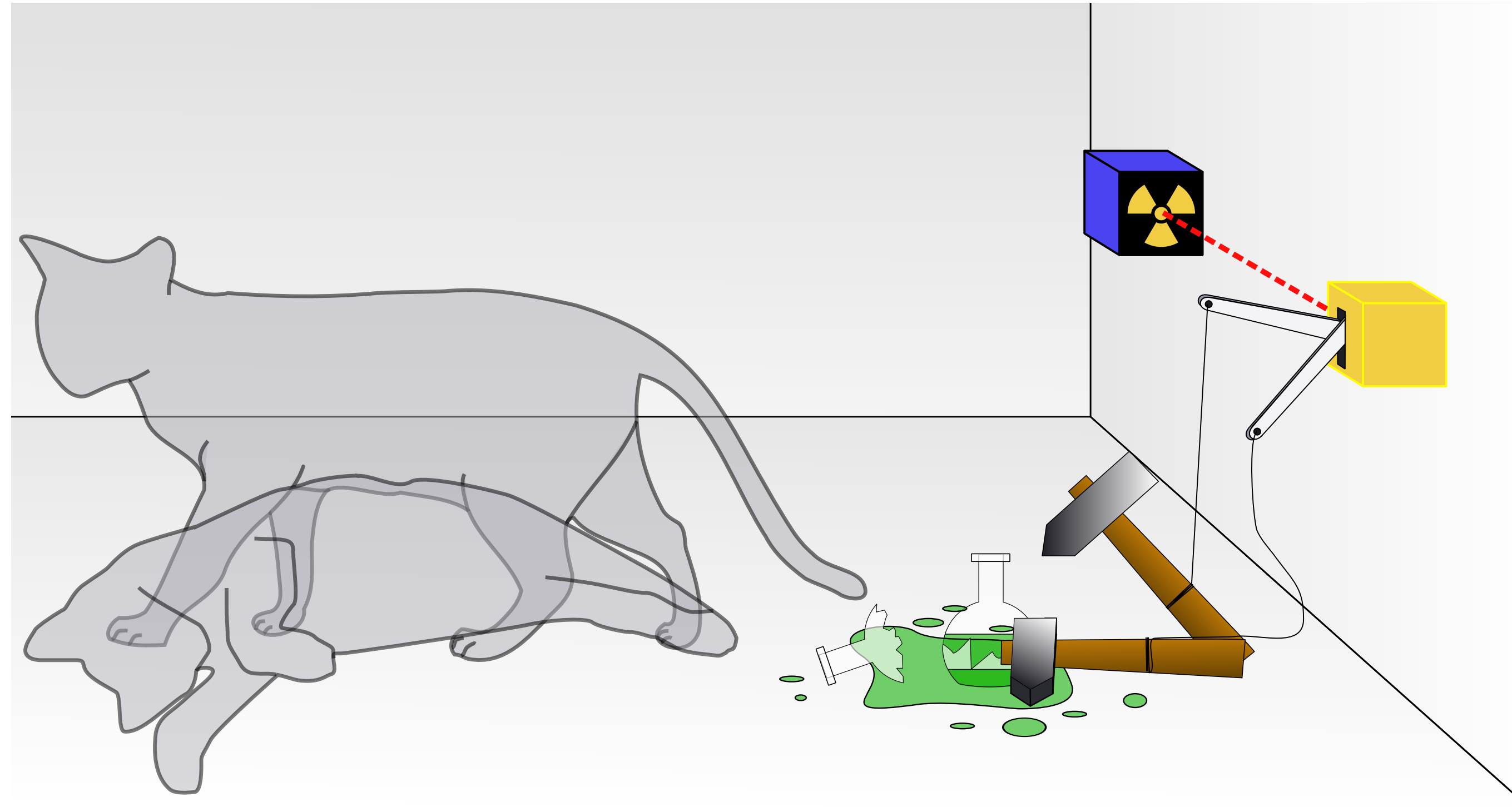
- $|c_m|^2$ can be thought of as weights in a weighted sum,

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

Measurement

- Immediately after the *measurement*, the state of the system will be Ψ_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



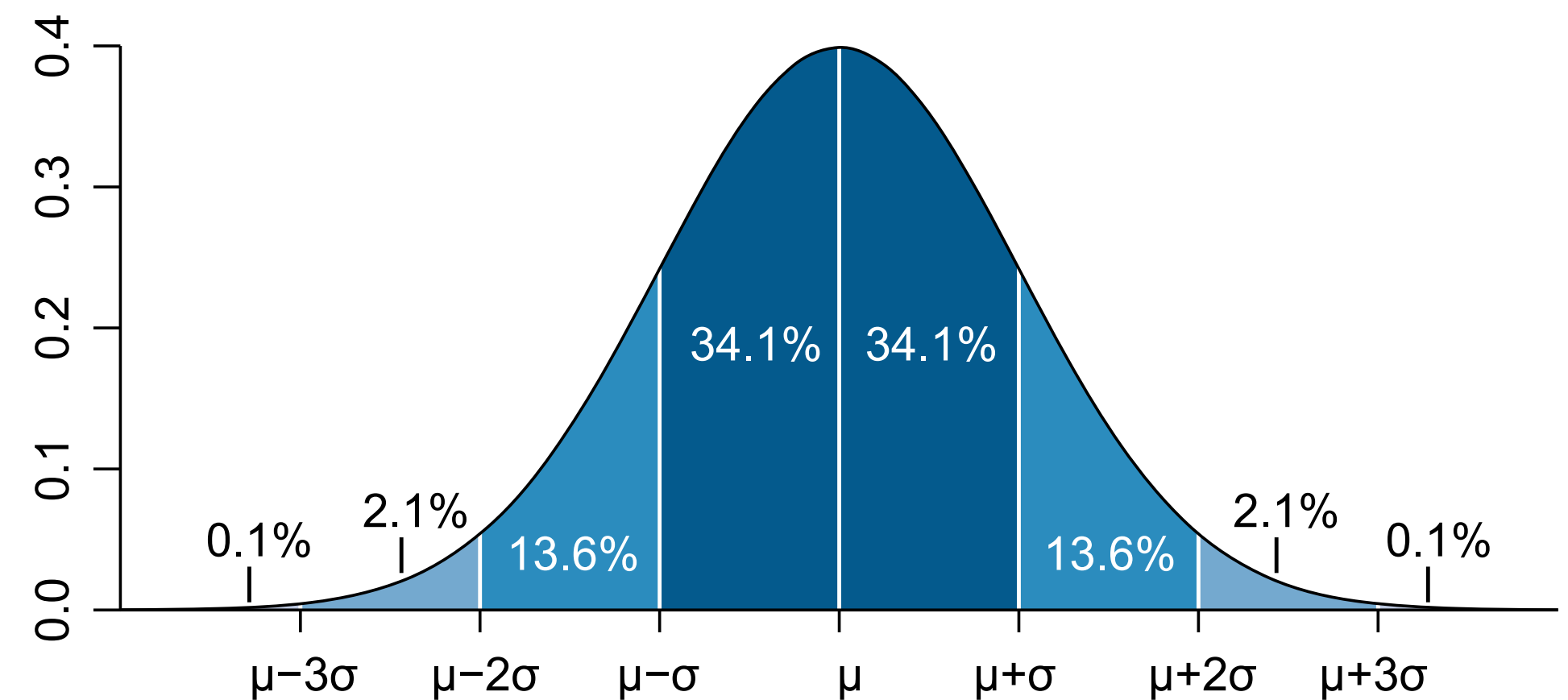
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Schrödinger's cat: a cat, a flask of poison, and a radioactive source connected to a Geiger counter are placed in a sealed box. As illustrated, the objects are in a state of superposition: the cat is both alive and dead.

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

PDF of a normal distribution



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

5. The equation for the wavefunction

- The wavefunction evolves in time according to the time-dependent Schrödinger equation, $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$
- 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, $\hat{H}\Psi = E\Psi$
- the focus of this class
- can be derived by separation of variables (will do so shortly)
- \hat{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
 - $T = \frac{p^2}{2m}$
 - In the position representation, $\hat{\mathbf{T}} = \frac{\hbar^2}{2m} \nabla^2$. $\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$.
- 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 $\hat{H}\Psi = E\Psi$

Separation of Variables, p. 1

- The Schrödinger equation is $\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$
- In one dimension, this is $-\frac{\hbar^2}{2m}\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi = i\hbar\frac{\partial\Psi}{\partial t}$
- 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 $-\frac{\hbar^2}{2m}\Theta\frac{\partial^2\Psi}{\partial x^2} + V(x)\Psi\Theta = i\hbar\Psi\frac{\partial\Theta}{\partial t}$

Separation of Variables, p. 2

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

Time Dependence

- One of the differential equations is $i\hbar \frac{\partial \Theta}{\partial t} = E\Theta$
- What is the solution of this differential equation?
- 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 \mathbf{r} is proportional to $|\Psi(\mathbf{r})|^2 d\tau$. Does the probability of the particle position depend on time?

Summary of Postulates

- The state of a system is fully described by a function $\Psi(r_1, r_2, \dots, t)$, 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 $\Psi = \sum c_m \Psi_m$, the probability of measuring a particular eigenvalue ω_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 $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$. If the potential energy is time-independent, then $\hat{H}\Psi = E\Psi$

Review

- What does a wavefunction describe?
- What are 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?