

# 8/24/2023

- 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  $\Psi(r_1, r_2, \dots, t)$ , 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  $\Psi$  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  $q$
- $i = \sqrt{-1}$
- $\hbar = \frac{h}{2\pi}$ , 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.

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

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



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

# Eigenfunction Expansions

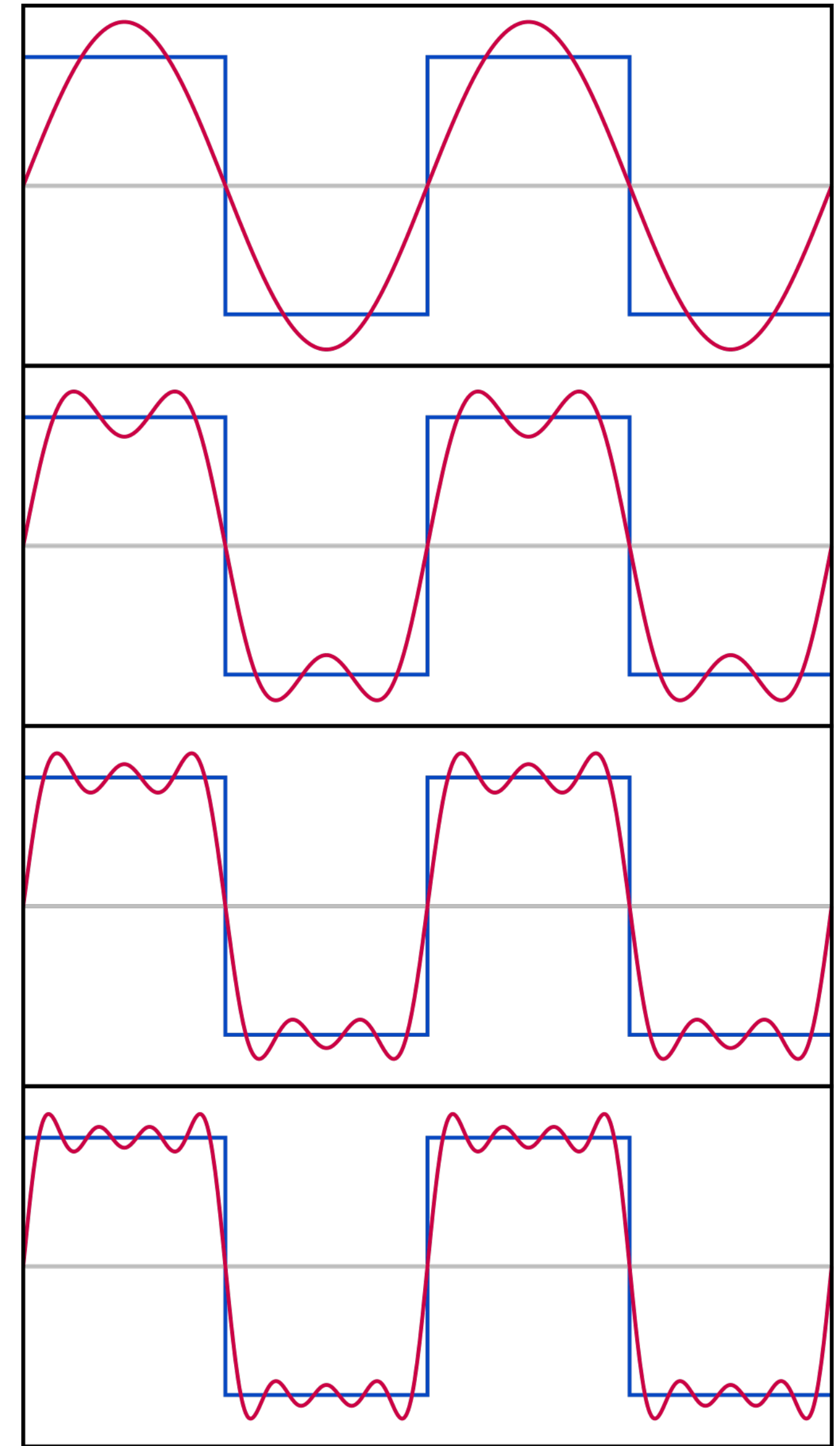
- Any function may be expressed as a linear combination of *all* the eigenfunctions of an operator,  $g = \sum_n c_n f_n$ .
- $c_n$  are coefficients
- $f_n$  are eigenfunctions. They are basis functions for  $g$ .

# Example Eigenfunctions

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

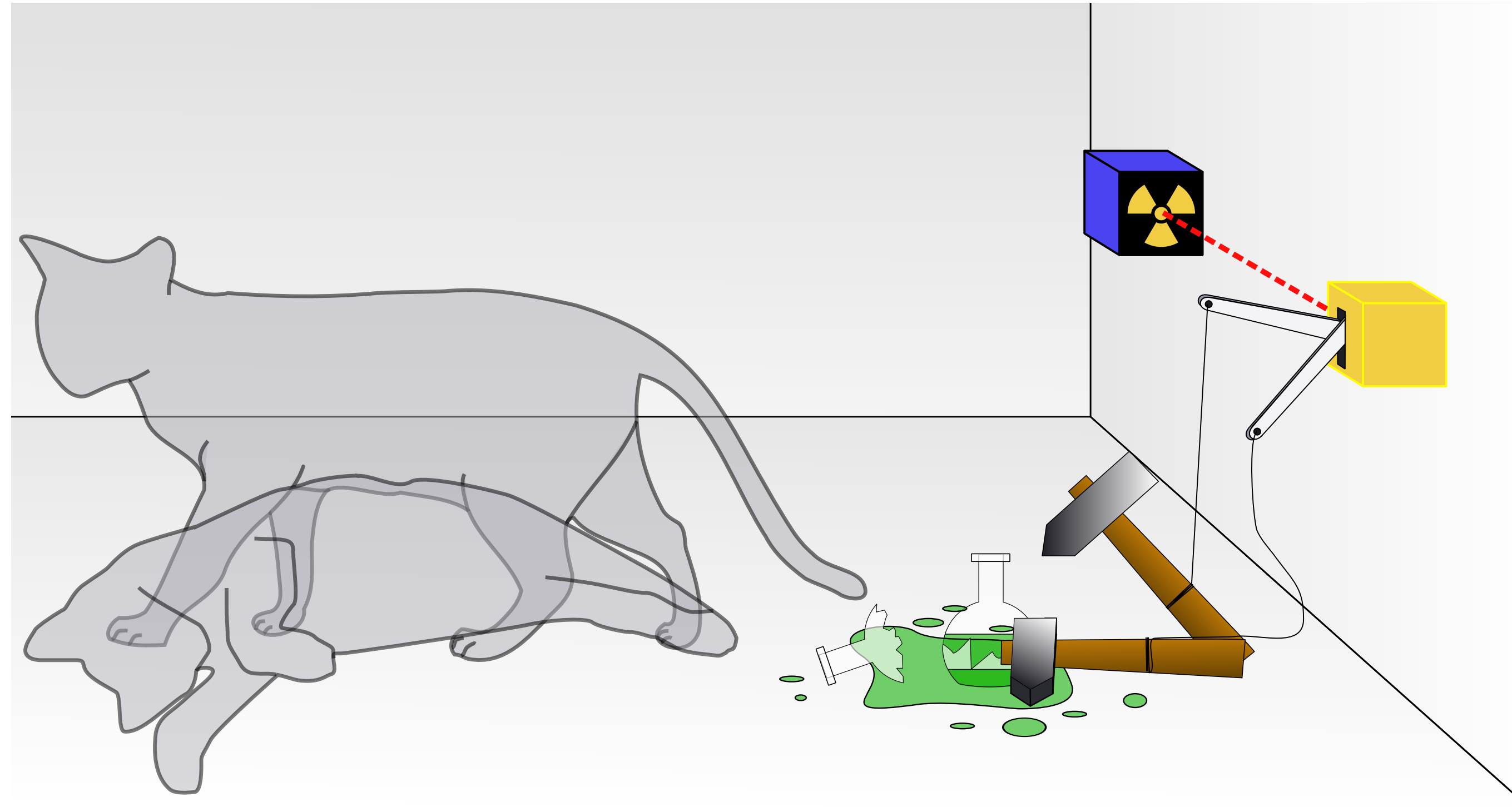
is proportional to  $|c_m|^2$ .

- $c_m$  is the coefficient
- $\Psi_m$  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  $\Psi_n$
- 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



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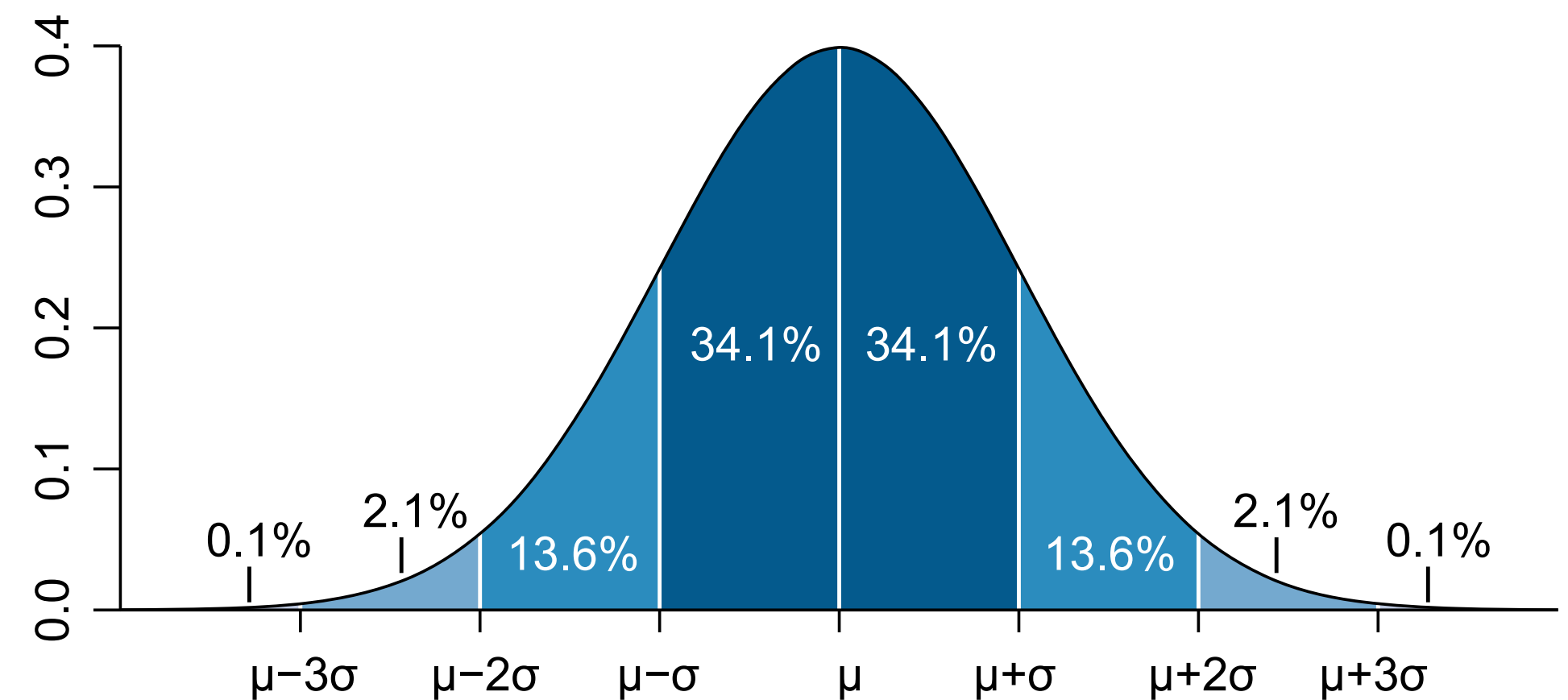
Schrödinger's cat: a cat, a flask of poison, and a radioactive source connected to a Geiger counter are placed in a sealed box. As illustrated, the objects are in a state of superposition: the cat is both alive and dead.



# 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
  - $$-\frac{\hbar^2}{2m} \frac{\partial^2 \Psi}{\partial x^2} + V(x)\Psi = \hat{H}\Psi = E\Psi$$
 Time-independent Schrödinger equation
  - $$i\hbar \frac{\partial \Theta}{\partial t} = E\Theta$$

# 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?
  - $\Theta = e^{-\frac{iE}{\hbar}t}$
- Thus if we have a solution for  $\hat{H}\Psi = E\Psi$ , 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  $\Psi(r_1, r_2, \dots, t)$ , 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  $\omega_n$  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  $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H}\Psi$ . 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?