

Lecture 2. Introduction to Quantum Mechanics

Physical Chemistry 1, Winter 2022

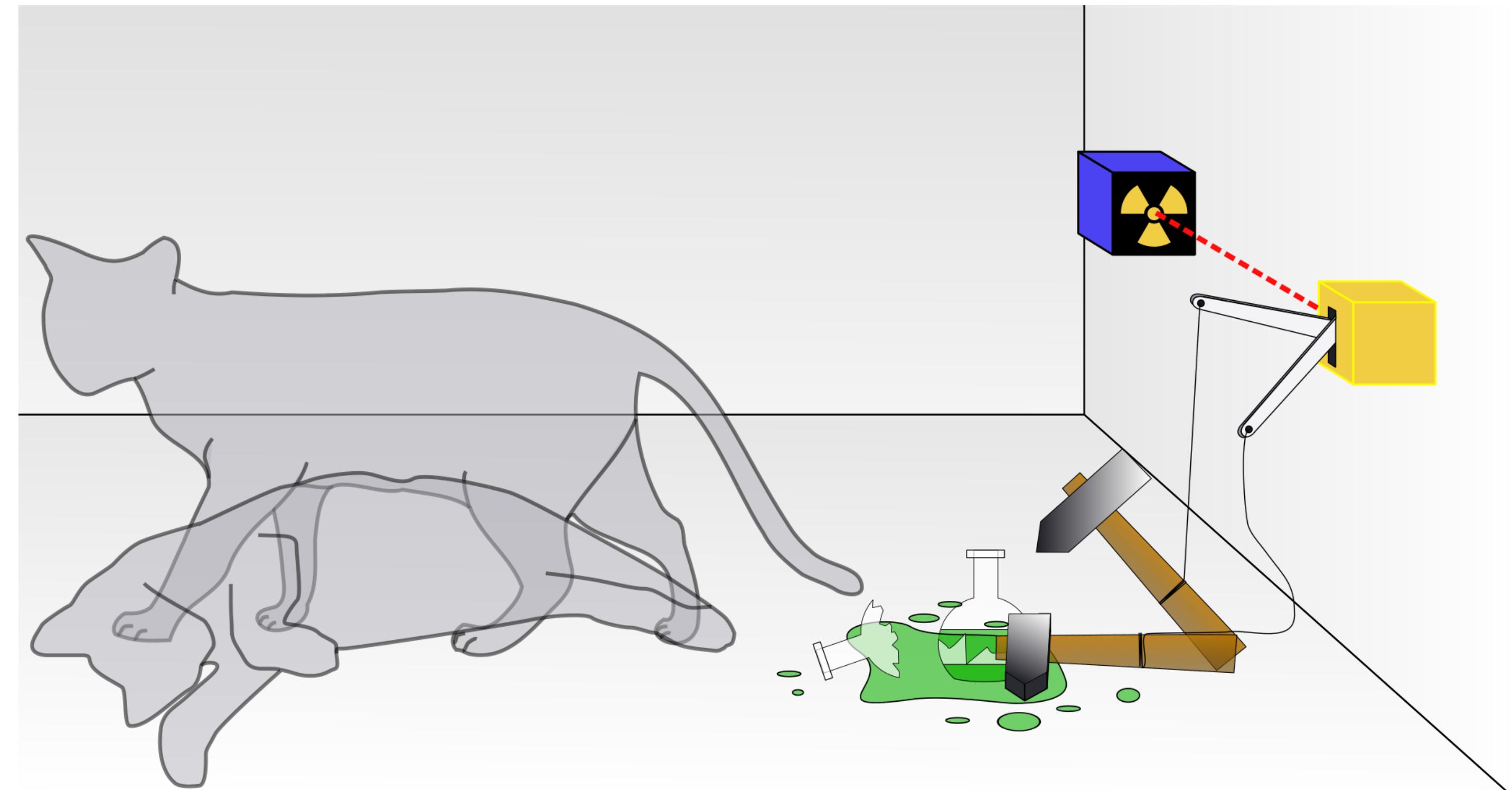
Department of Chemistry

Jiho Son

Seoul National University

Schrödinger's cat

“The thought experiment”. Let’s try to understand this experiment.



Retrieved from Wikipedia

Why do we need quantum mechanics?

In classical mechanics, knowing the initial condition of the object (such as initial configuration and velocity) determines the trajectory via *Newton's 2nd law*, or equivalently, *Hamilton's equation of motion*.

$$\mathbf{F} = m\mathbf{a} \quad \frac{\partial H}{\partial p_i} = \dot{q}_i, \quad \frac{\partial H}{\partial q_i} = -\dot{p}_i$$

In atomic scale, classical things you know does not work anymore.

Bizarre things occur in atomic scale, as you had seen in last lecture.

Why do we need quantum mechanics?

In microscopic world, objects follow new equation of motion called *Schrödinger's equation*:

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V\psi = E\psi, \quad \hat{H}\psi = E\psi$$

where H is called the **Hamiltonian** operator. Let's dive into the world of quantum mechanics.

You are now learning a new language of nature.

When you learn a new language, you should not complain why apple is called “apple”.

Operators

In quantum mechanics, everything is **linear operators**.

Operator operates on operand function, to yield some other function. We put hat sign on operators.

$$\hat{A} = \frac{d}{dx}, \quad \hat{A}x^2 = 2x$$

An operator is **linear** if it satisfies following properties.

$$\hat{A}(f_1 + f_2) = \hat{A}f_1 + \hat{A}f_2$$

$$\hat{A}(cf) = c\hat{A}f$$

Of course, there are nonlinear operators, i.e., $\hat{B}f = \sqrt{f}$

Operators

All observables in classical mechanics has its quantum-mechanical counterpart, *operators*.

For example, operator for the position is very simple.

$$\hat{x}f = xf$$

It is simply multiplying x . Operator for the momentum is a differentiation. (why?)

$$\hat{p} = -i\hbar \frac{d}{dx}, \quad \hat{\mathbf{p}} = -i\hbar \nabla$$

Therefore operator for kinetic energy is

$$\frac{\hat{p}^2}{2m} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2}, \quad \frac{\hat{\mathbf{p}}^2}{2m} = -\frac{\hbar^2}{2m} \nabla^2$$

Hamiltonian operator

Operator for potential energy is simply multiplication.

$$\hat{V}(\mathbf{r})f = V(\mathbf{r})f$$

Therefore, operator for total mechanical energy, which is called **Hamiltonian**, has following form.

$$\hat{H} = -\frac{\hat{\mathbf{p}}^2}{2m} \nabla^2 + \hat{V}(\mathbf{r})$$

All other quantities, such as angular momentum, velocity, etc. can be transformed into quantum-mechanical version if you know quantum-mechanical form of position and momentum operator.

Eigenvalue equation

Let's go back to the Schrödinger equation.

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

Hamiltonian operator operated on some function psi yields some constant, E , and gives psi again.

This form of equation is called an **eigenvalue equation**.

The function psi is called an **eigenfunction**, and the value E is called an **eigenvalue**.

Digression. You must be familiar with these glossaries if you studied linear algebra before.

The wavefunction

In summary, by solving the Schrödinger equation, one can obtain *energy eigenvalues* and **wavefunction**.

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

The state of a quantum-mechanical system is *completely* specified by a wavefunction. All possible information about the system can be derived from wavefunction.

Note that the Hamiltonian consists of kinetic energy part and potential energy part. Form of kinetic energy term is invariant. Therefore, form of potential energy specifies system.

Given potential energy, solving Schrödinger equation gives us total information about the system.

The Schrödinger Equation

The one-dimensional Schrödinger equation is

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

Yes, this is second-order ordinary differential equation (ODE). (Yes you **should** solve differential equations)

Three-dimensional case is even worse.

$$-\frac{\hbar^2}{2m} \nabla^2 \psi + V(\mathbf{r})\psi = E\psi$$

Second derivative becomes Laplacian here: Hence, Schrödinger equation is a PDE. Form of the Laplacian operator changes under your choice of coordinate system: Cartesian, cylindrical, spherical, etc.

Math: Simple ODE

Consider simple ODE, where k is a positive constant.

$$\frac{d^2 f(x)}{dx^2} = -k^2 f(x)$$

What kind of function returns to itself after differentiating twice?

Trigonometric functions.

If you thought e^{ikx} , that is also an answer. More on this later, if possible.

Math: Simple ODE

Therefore, possible solutions are: $f(x) = \sin kx$ or $\cos kx$

These are called **special solution** of DE. Note that differentiation operator is linear.

Therefore, linear combination of special solutions are also solution of DE. This is a **general solution**.

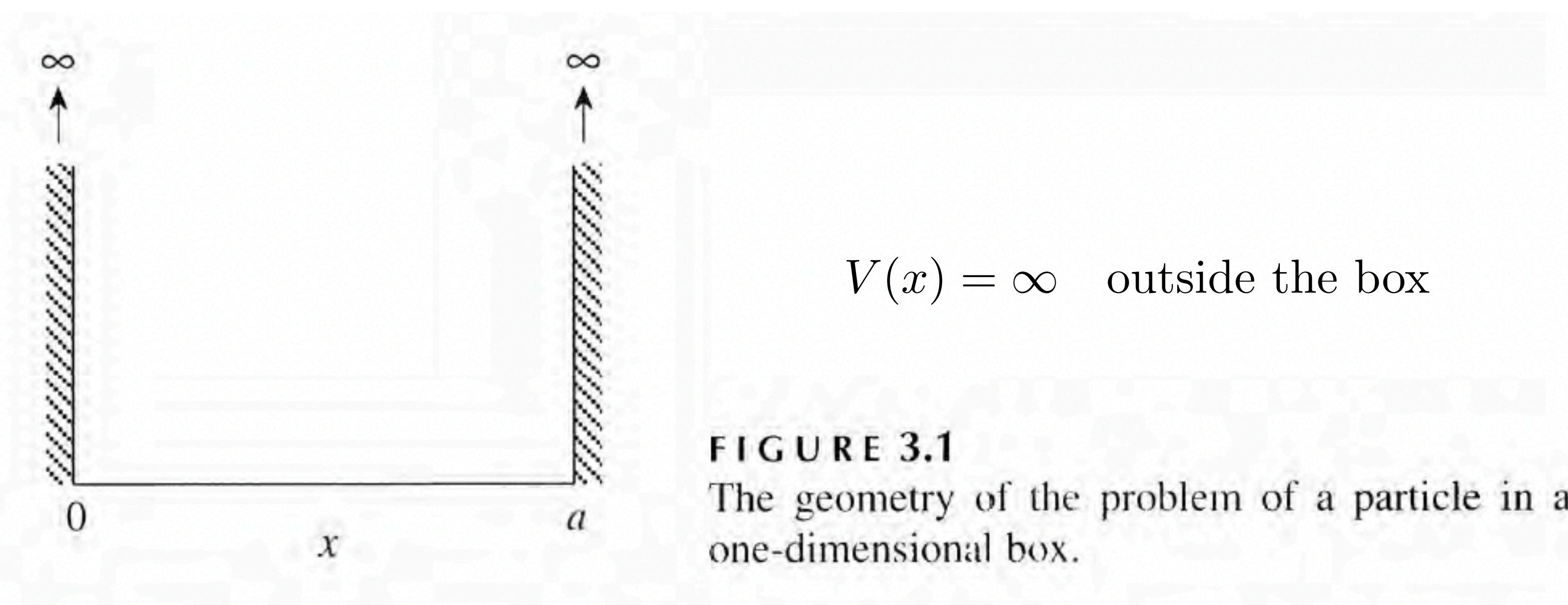
$$f(x) = A \sin kx + B \cos kx$$

However, we still have undetermined constants A and B in the general solution.

Constraints that specifies these constants are called **boundary conditions**.

Particle in a box

Let's solve a toy model called *particle in a box*, in order to get familiar with quantum mechanics.



This is very simple situation. A particle is confined inside a one-dimensional box of length a .

There is no potential energy inside the box, which means $V(x) = 0$ for $0 \leq x \leq a$

Particle in a box

Therefore, inside the box, potential energy term vanishes. Schrödinger equation is:

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

Rearrange terms, then you find the familiar ODE.

$$\frac{d^2\psi}{dx^2} = -\frac{2mE}{\hbar^2}\psi \equiv -k^2\psi \quad \left(E = \frac{\hbar^2 k^2}{2m}\right)$$

General solution follows, but how can we decide the unknown constants?

$$\psi(x) = A \sin kx + B \cos kx$$

Boundary conditions

In case of *particle-in-a-box* problem, wavefunction outside the box should vanish. (why?)

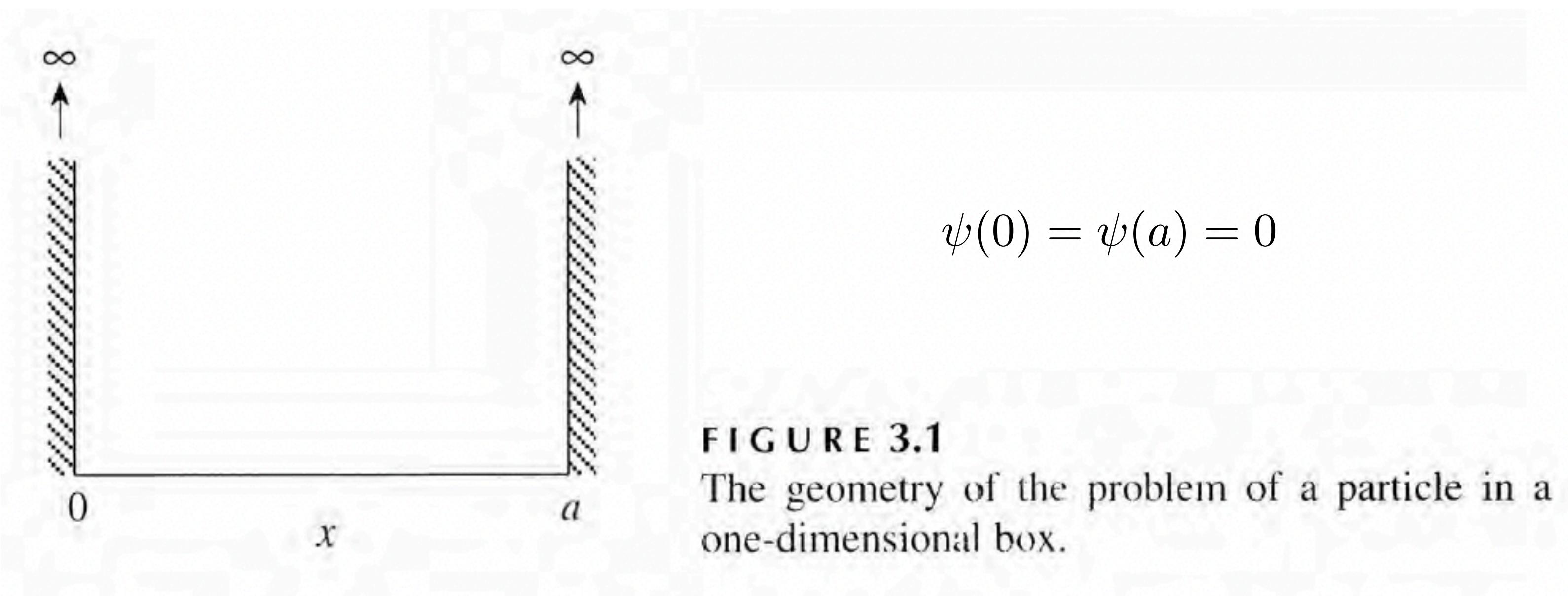


FIGURE 3.1

The geometry of the problem of a particle in a one-dimensional box.

Digression. For the *physical* wavefunction, first derivative of wavefunction should be finite, single-valued, and continuous.

Boundary conditions

From the boundary conditions,

$$\psi(0) = A \sin 0 + B \cos 0 = 0 \implies B = 0$$

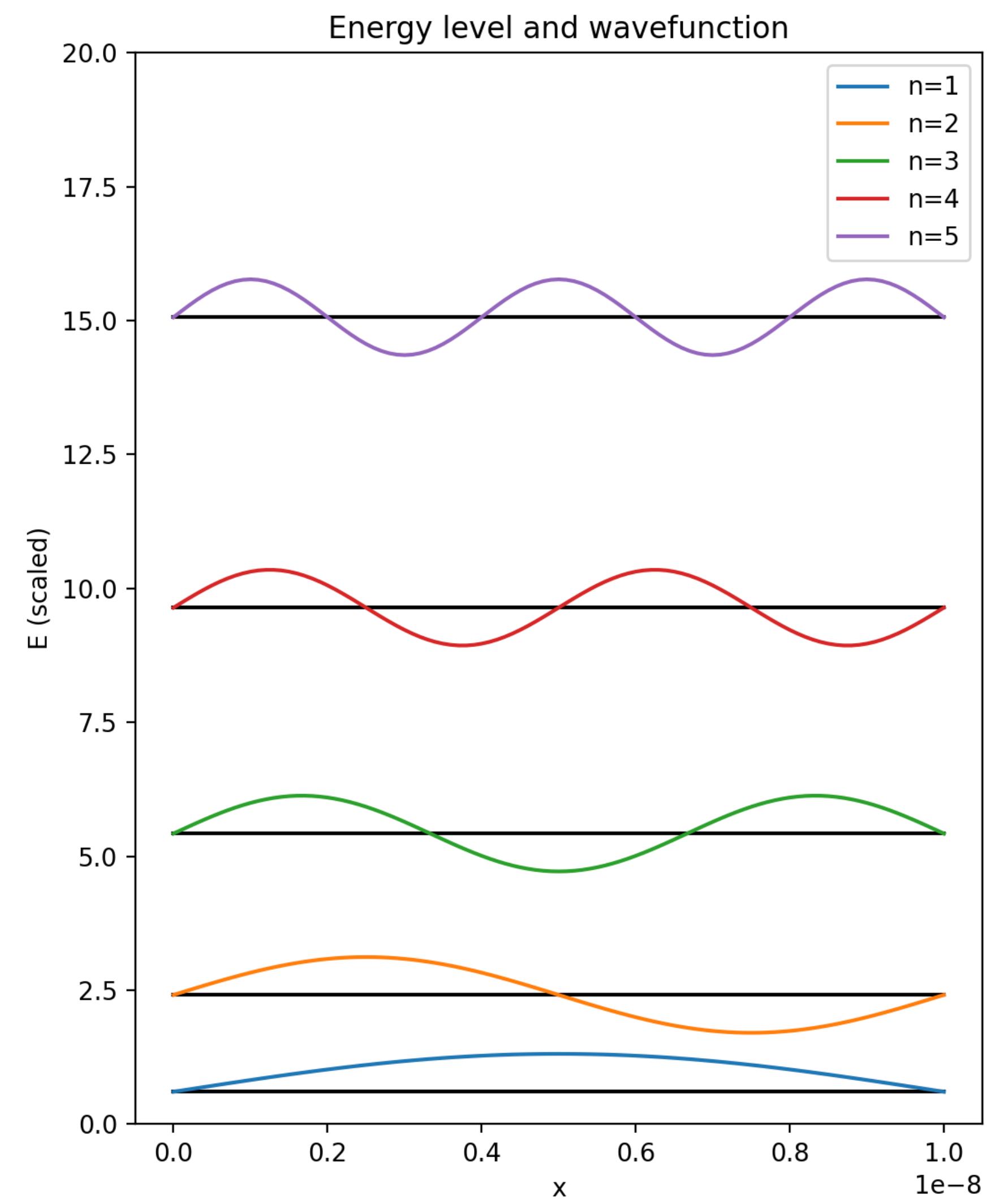
$$\psi(a) = A \sin ka = 0 \implies ka = n\pi \quad (n = 1, 2, 3, \dots)$$

Therefore eigenfunctions and eigenvalues are

$$\psi_n(x) = A \sin \frac{n\pi x}{a} \quad (n = 1, 2, 3, \dots)$$

$$E_n = \frac{\hbar^2 k_n^2}{2m} = \frac{n^2 \pi^2 \hbar^2}{2ma^2} = \frac{n^2 \hbar^2}{8ma^2} \quad (n = 1, 2, 3, \dots)$$

Note that (1) energy is *quantized* and (2) we still have one undetermined constant.



Born interpretation

The Born interpretation gives us a physical interpretation of wavefunctions.

$$\psi^*(x)\psi(x) dx$$

The product of wavefunction and its *complex conjugate* becomes the **probability density function**. Hence, $\psi^*(x)\psi(x) dx$ denotes the probability to find a particle between the interval $x \sim x+dx$.

Probability distribution functions should be **normalized**, i.e., integrating the probability density on all possible x values should yield 1.

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

Particle in a box

From the normalization condition,

$$|A|^2 \int_0^a \sin^2 \frac{n\pi x}{a} dx = \frac{|A|^2}{2} \int_0^a \left(1 - \cos \frac{2n\pi x}{a}\right) dx = \frac{|A|^2}{2} a = 1 \implies |A| = \sqrt{\frac{2}{a}}$$

The solution of particle in a box problem is:

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin \frac{n\pi x}{a} \quad (n = 1, 2, 3, \dots)$$

Particle in a box

Things to note.

- I. *Quantization* arises while we are solving the differential equation.
- II. Nodes (point where wavefunction = 0). Probability to find the particle is also zero there. Number of nodes increase as the energy level increases.
- III. If you want to evaluate the probability to find the particle in the left half of the box ($0 \leq x \leq a/4$), just integrate the probability distribution function in that range! (Do it yourself at home)

$$\int_0^{a/4} \psi_n^*(x) \psi_n(x) dx = \frac{1}{2} \quad (\text{regardless of } n)$$

More quantum mechanics

Now we have solved the simplest toy model we can deal with. So what now?

Let's dive in a little bit more. Before we do so, we need more mathematics.

Math: Basis

In linear algebra, a basis B of a finite-dimensional vector space V over a field F is a linearly-independent subset of V that **spans** V . If $\mathbf{v}_1, \mathbf{v}_2, \dots, \mathbf{v}_n$ are basis vectors of V , then

$$c_1\mathbf{v}_1 + \cdots + c_n\mathbf{v}_n = 0 \text{ implies } c_1 = \cdots = c_n = 0$$

$$\forall \mathbf{w} \in V, \exists a_1, \dots, a_n \text{ such that } \mathbf{w} = a_1\mathbf{v}_1 + \cdots + a_n\mathbf{v}_n$$

This concept can be expanded to *functions*.

Note that two vectors are orthogonal if their inner product is zero.

Math: Basis

For example, we can expand certain functions* into the linear combination of sine functions.

$$f(x) = \sum_{n=0}^{\infty} c_n \sin nx$$

Certain set of functions can express *function space*. These are called the basis functions.

In most cases, basis functions are mutually orthogonal. If two functions are orthogonal, their inner product is zero. Inner product of two functions are defined as follows.

$$\langle f, g \rangle = \int f^*(x)g(x) dx$$

Math: Hermitian operators

Let's introduce **Dirac notation**.

$$\int f^*(x)g(x) dx = \langle f|g\rangle, \quad \int f^*(x)\hat{A}g(x) dx = \langle f|\hat{A}|g\rangle$$

An operator is **Hermitian** if

$$\int f^*(x)\hat{A}g(x) dx = \int g(x)[\hat{A}f(x)]^* dx, \quad \langle f|\hat{A}g\rangle = \langle \hat{A}f|g\rangle$$

All operators in quantum mechanics are Hermitian. We measure “real number”.

Therefore, Hermitian operators should have **real** eigenvalues.*

Math: Hermitian operators

Theorem. Eigenfunctions of Hermitian operators are orthogonal.

Let's assume that all eigenvalues are different. $\hat{A}\psi_n = a_n\psi_n$

$$\langle \psi_m | \hat{A} \psi_n \rangle = a_n \langle \psi_m | \psi_n \rangle$$

$$\langle \psi_n | \hat{A} \psi_m \rangle = a_m \langle \psi_n | \psi_m \rangle \implies \langle \psi_n | \hat{A} \psi_m \rangle^* = a_m \langle \psi_m | \psi_n \rangle$$

Since A is Hermitian, two terms are equivalent.

Eigenvalues a_m and a_n are different unless $m=n$. Therefore

$$\langle \psi_m | \psi_n \rangle = \delta_{mn}$$

If one includes the normalization condition.

Math: Hermitian operators

Therefore, **eigenfunctions of Hermitian operators constructs orthogonal basis.**

In other words, if we find any solutions of Schrödinger equation, it constructs orthogonal basis.

In other words (again), arbitrary function can be expressed with the linear combination of $\{\psi_n\}_{n=1}^{\infty}$!

Conclusion. Eigenfunctions of quantum-mechanical operators are *complete*.

Digression. If you know linear algebra, ...

understanding these arguments can be done in the analogy of **Hermitian matrices**.

More quantum mechanics

Now we have solved the simplest toy model we can deal with. So what now?

Let's dive in a little bit more.

Measurements

If we “act” an operator to the wavefunction, it yields wavefunction itself and some value.

This is a measurement.

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

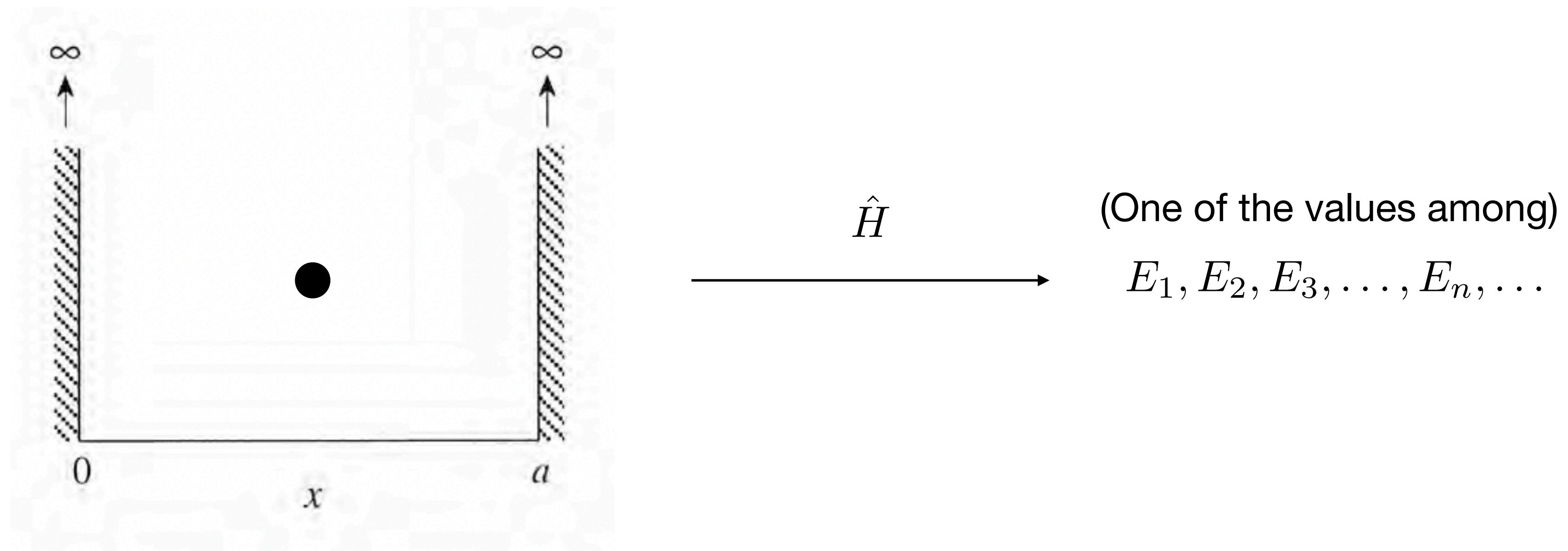
Therefore only eigenvalues of the operator can be measured.

(Other values are forbidden: quantization!)

Measurements

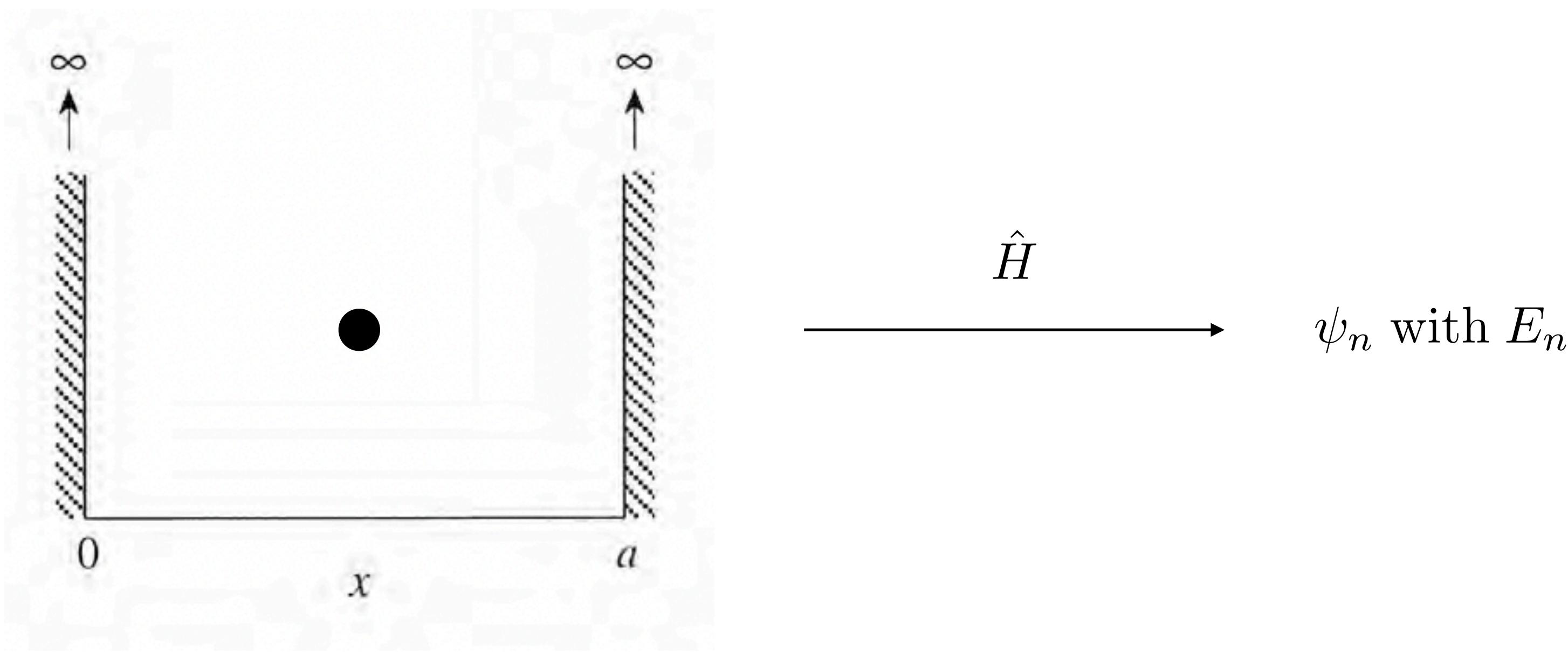
For example, if we measure the energy of a particle inside a box, we can only obtain one of the E_n values.

Note that the operator related to the energy is Hamiltonian.



Measurements

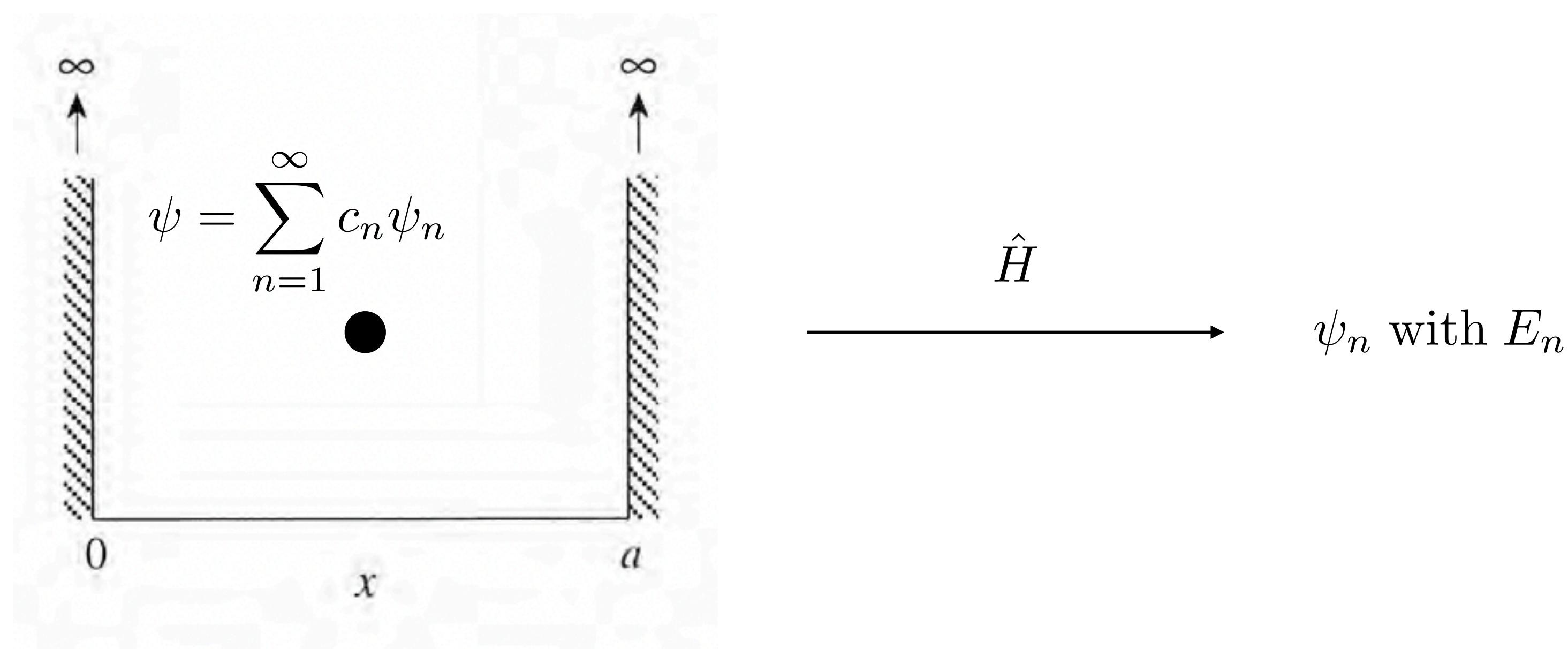
In other words, if energy E_n is measured it means that the particle is in ψ_n state.



Q. What was the wavefunction, before the energy measurement?

Measurements

The answer is, **we don't know**.

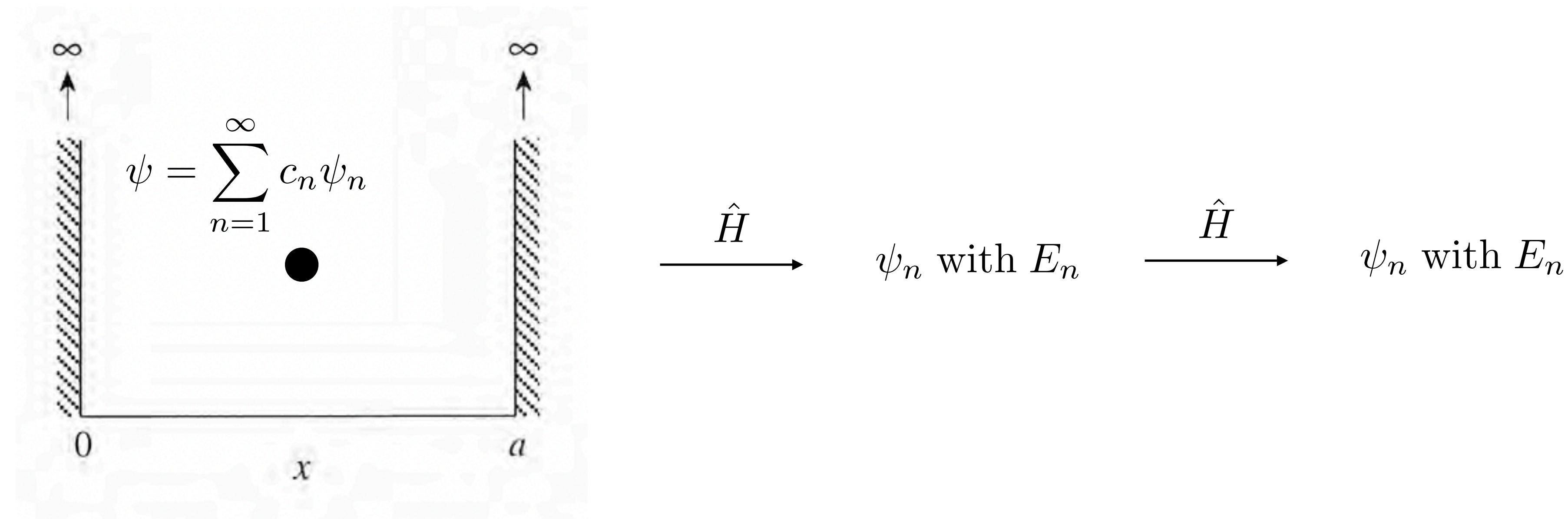


The previous state is unknown (somewhat wavefunction we do not know).

When we **measure** energy, wavefunction **collapses** into one of the eigenstates.

(Multiple) Measurements

Suppose that we measure the energy once again.



After the first measurement, system remains in n-th eigenstate.

Sequential measurement does not alter the eigenstate, hence same energy is observed.

Math: Commutator

Changing orders of operators cannot be done arbitrarily. In general,

$$\hat{A}\hat{B} \neq \hat{B}\hat{A}$$

Commutator of two operator is defined as

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A}$$

If two operators *commute*, then commutator is zero. Note that

$$[\hat{B}, \hat{A}] = -[\hat{A}, \hat{B}]$$

Commutator is *antisymmetric*.

Math: Commutator

Two commuting operators are in special relation.

Theorem. If two operators commute, they *share* common set of eigenfunctions.

(Proof) Let $[\hat{A}, \hat{B}] = 0$ and $\hat{A}\psi_n = a_n\psi_n$, $\hat{B}\phi_n = b_n\phi_n$. Then

$$\hat{A}\hat{B}\phi_n = \hat{B}\hat{A}\phi_n = b_n\hat{A}\phi_n$$

So, $\hat{A}\phi_n$ is an eigenfunction of operator B with eigenvalue b_n . Hence it should be a constant time of ϕ_n .

$$\hat{A}\phi_n = C_n \cdot \phi_n$$

From this equation, we showed that eigenfunctions of B are also eigenfunctions of A .

Math: Commutator

For example, momentum and kinetic energy operator commutes.

$$[p_x, \frac{p_x^2}{2m}] = 0$$

Therefore momentum and kinetic energy operator share eigenstates.

However, position and momentum do not.

$$[\hat{x}, \hat{p}]f = \hat{x}\hat{p}f - \hat{p}\hat{x}f = x \cdot \left(-i\hbar \frac{d}{dx} f \right) + i\hbar \frac{d}{dx}(xf) = i\hbar f$$

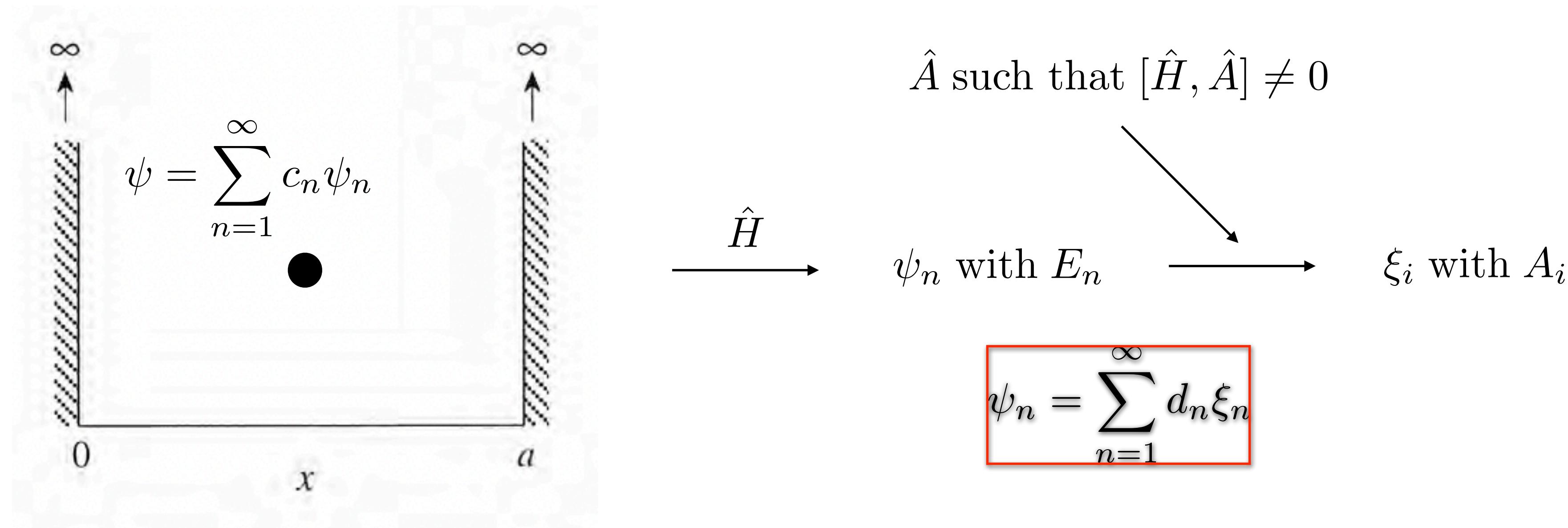
This commutator is the most fundamental one: **canonical commutator**.

$$[\hat{x}, \hat{p}] = i\hbar$$

Measurement (again)

Suppose that we measure two non-commuting observables sequentially.

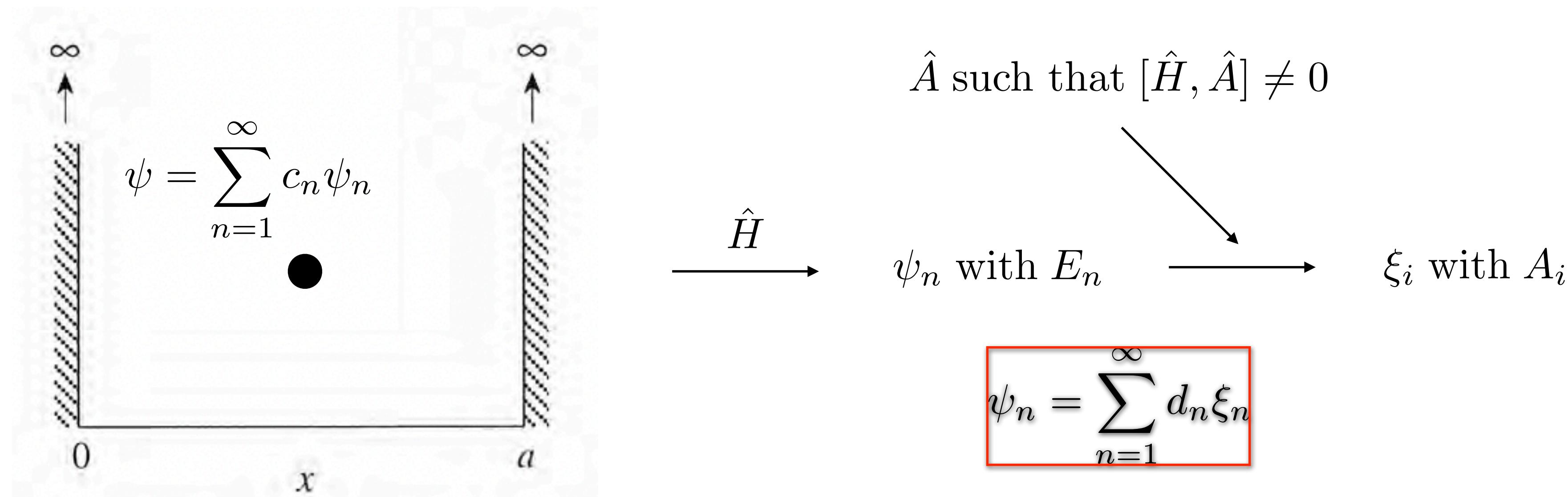
After the first measurement, the system collapses into certain eigenstate of Hamiltonian (for here).



Measurement (again)

Since they do not commute, they do not share eigenfunctions (or *different basis*).

Though ψ_n was an eigenstate for energy, for A , it is another random superposition of “eigenstates of A ”.



Therefore state collapses again, into some eigenstate ξ_i .

If you measure energy again, it does not give E_n : state collapses randomly.

Schrödinger's cat

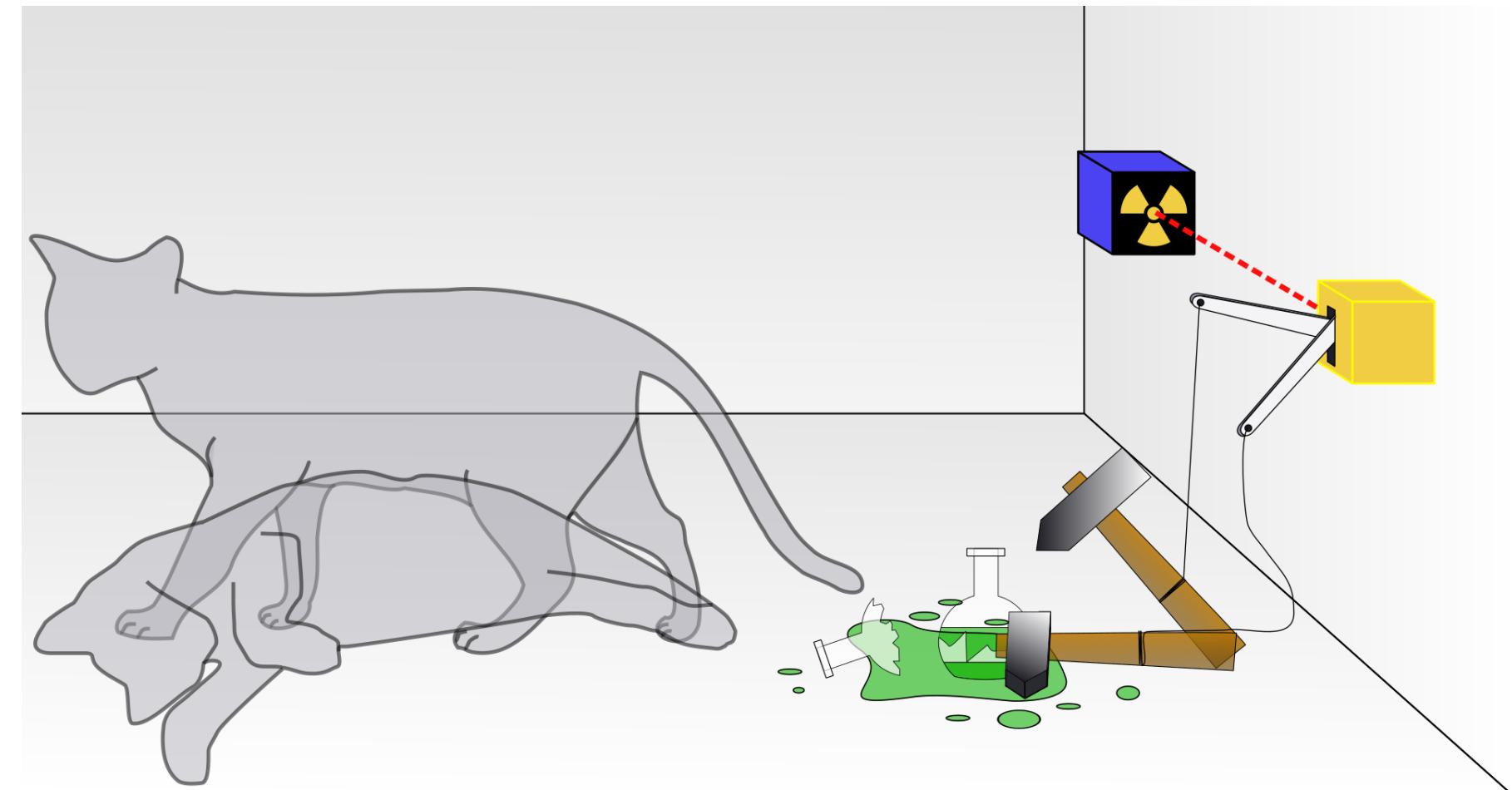
Define life operator, whose eigenvalue is +1 when the cat is alive. If dead, eigenvalue is -1.

$$\hat{L} |\text{cat}\rangle = \pm |\text{cat}\rangle$$

$$\hat{L} |\text{live}\rangle = +|\text{live}\rangle, \hat{L} |\text{dead}\rangle = -|\text{dead}\rangle$$

Before the observation, we do not know whether the cat is alive or not. Therefore, it exists as a superposition.

$$\frac{1}{\sqrt{2}}[|\text{live}\rangle + |\text{dead}\rangle]$$



Retrieved from Wikipedia

After the observation, we measure whether the cat is alive or not. Then wavefunction collapses into one eigenstate.

References of this lecture

If you are interested in more quantum mechanics exercises,

Griffiths, D. J.; Schroeter, D. F. *Introduction to Quantum Mechanics*, 3rd ed.; Cambridge University Press, 2018.

If you are interested in more robust, linear-algebra like introduction to theoretical framework of quantum mechanics,

Shankar, R. *Principles of Quantum Mechanics*, 2nd ed.; Springer, 1994.

Atkins' Physical Chemistry textbook is always your companion, even though I do not mention it.