

2021.06.28

Lecture 3



서울대학교
SEOUL NATIONAL UNIVERSITY

Department of Chemistry

PChem 2

Physical Chemistry 2

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Physical Chemistry 2

Lecture 3. Postulates of Quantum Mechanics

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Topics in Lecture 3

Postulates of quantum mechanics

Operators

Eigenvalue equations and expectation values

Hermitian operator

Dirac notation

In Atkins' *Physical Chemistry* (11th ed.),

7C Operators and Observables

Main Reference for this lecture

Donald A. McQuarrie, John D. Simon

Physical Chemistry: A Molecular Approach (2nd ed.), University Science Books (1997).

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Wavefunction

Postulate 1

The state of a quantum-mechanical system is completely specified by a function $\psi(x)$ that depends upon the coordinate of the particle. All possible information about the system can be derived from $\psi(x)$. This function, called the wave function or the state function, has the important property that $\psi^*(x)\psi(x)dx$ is the probability that the particle lies in the interval dx , located at the position x .

Normalization

The total probability of finding a particle somewhere must be unity, thus

$$\int_{\text{all space}} |\psi(x)|^2 dx = 1$$

Usually, we write the *volume element* as $d\tau$.

$$\int_{\text{all space}} |\psi|^2 d\tau = 1$$



Operators

An *operator* is a mathematical operation on a function, transforming it into another.

$$\hat{A}f(x) = g(x)$$

For example,

$$\hat{A} = \frac{d}{dx} \implies \hat{A}f(x) = \frac{df}{dx}, \quad \hat{B} = a \implies \hat{B}f(x) = af(x)$$

In quantum mechanics, our main interest is on *linear operators*, which satisfy

$$\hat{A}(f + g) = \hat{A}f + \hat{A}g, \quad \hat{A}(af) = a\hat{A}f$$

The sum of operators is intuitive: $(\hat{A} + \hat{B})f = \hat{A}f + \hat{B}f$

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Operators

Sequential apply of operators is similar with composition of functions.

$$\hat{A}\hat{B}f(x) = \hat{A} \left(\hat{B}f(x) \right)$$

In general, $\hat{A}\hat{B} \neq \hat{B}\hat{A}$. If $\hat{A}\hat{B} = \hat{B}\hat{A}$, \hat{A} and \hat{B} *commute*.

Define *commutator*

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

If two operators commute, then commutator is zero.

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

Product of operators $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} + \hat{B}[\hat{A}, \hat{C}]$

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

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Operators

Postulate 2

To every observable in classical mechanics there corresponds a linear operator in quantum mechanics.

Observables		Operator	
Position	x, \mathbf{r}	$\hat{x}, \hat{\mathbf{r}}$	Multiply by x, \mathbf{r}
Momentum	p_x, \mathbf{p}	$\hat{p}_x, \hat{\mathbf{p}}$	$-i\hbar \frac{\partial}{\partial x}, -i\hbar \nabla$
Kinetic energy	K_x, K	\hat{K}_x, \hat{K}	$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2}, -\frac{\hbar^2}{2m} \nabla^2$
Potential energy	$V(x), V(x, y, z)$	$\hat{V}(x), \hat{V}(x, y, z)$	Multiply by $V(x, y, z)$
Total energy	E	\hat{H}	$-\frac{\hbar^2}{2m} \nabla^2 + V(x, y, z)$
Angular momentum	$L_x = yp_z - zp_y$ $L_y = zp_x - xp_z$ $L_z = xp_y - yp_x$	$\hat{L}_x, \hat{L}_y, \hat{L}_z$	$\hat{L}_x = -i\hbar \left(y \frac{\partial}{\partial z} - z \frac{\partial}{\partial y} \right)$



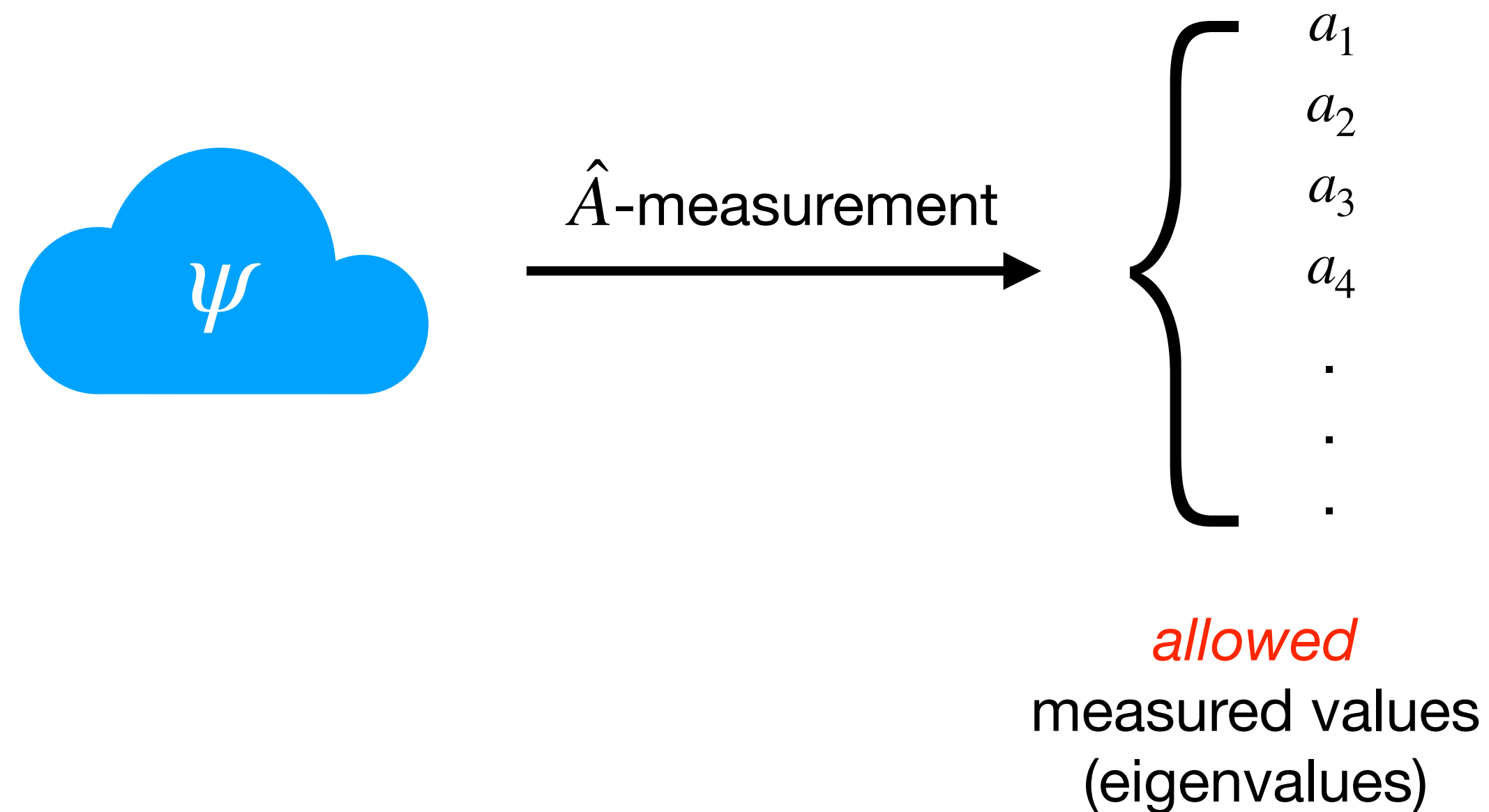


Eigenvalue equation

Postulate 3

In any measurement of the observable associated with the operator \hat{A} , the only values that will ever be observed are the eigenvalues a_n , which satisfy the eigenvalue equation

$$\hat{A}\psi_n = a_n\psi_n$$





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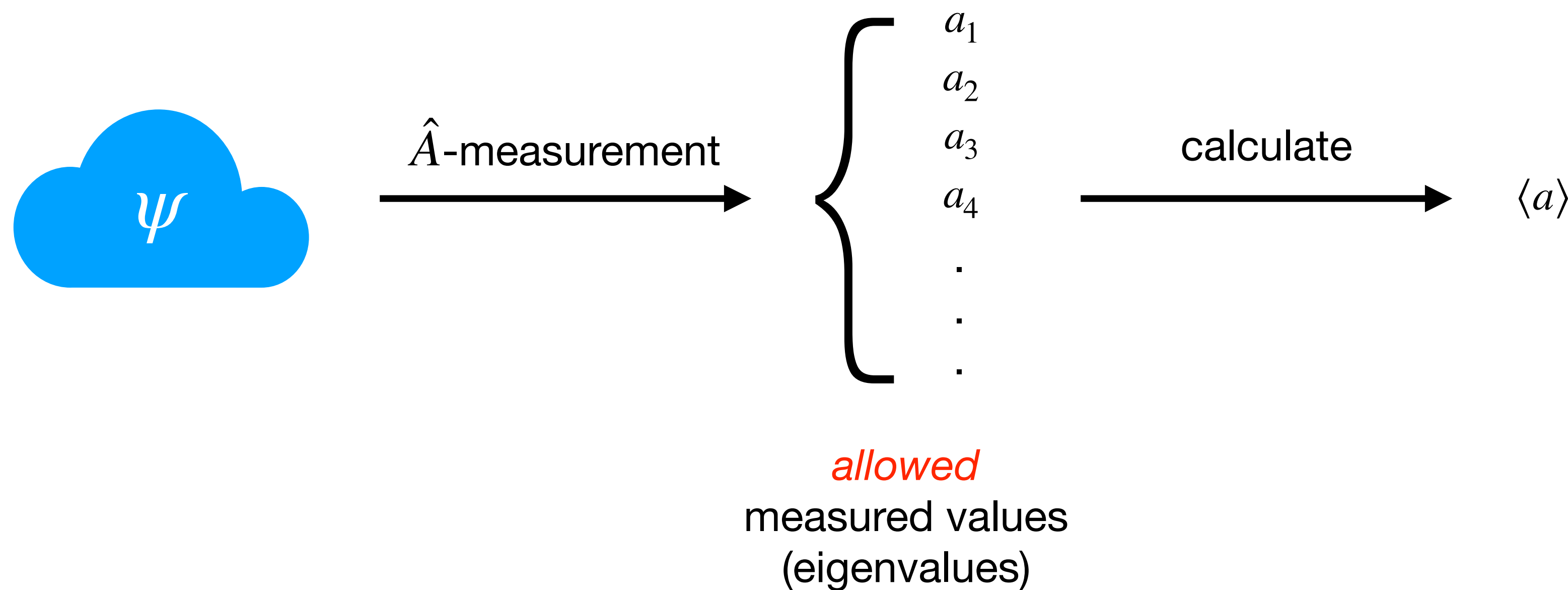
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Expectation values

Postulate 4

If a system is in a state described by a normalized wave function ψ , then the average value of the observable corresponding to \hat{A} is given by

$$\langle a \rangle = \int_{\text{all space}} \psi^*(x) \hat{A} \psi(x) dx$$



Expectation values

Meaning of postulate 4

When we measure specific observable A , we can only observe a_n 's, which are eigenvalues of \hat{A} .
We cannot predict the observation result of each measurement, but can calculate expectation value.

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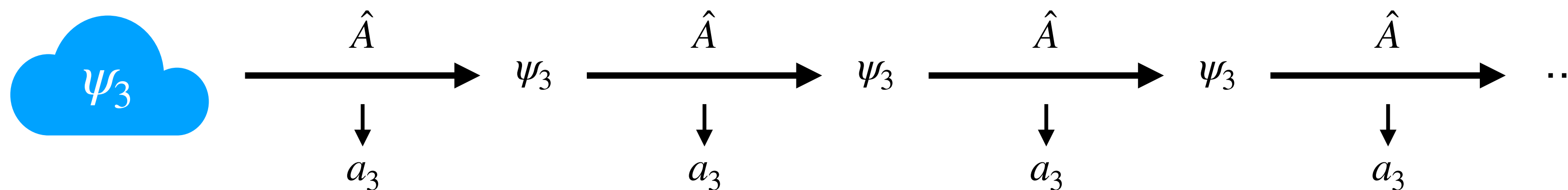
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Expectation values

Measurement

If the system is originally at a ψ_n , which is an eigenfunction, measurements always gives the same value a_n . In this case, uncertainty of measurement is zero.



$$\langle a \rangle = \int \psi_3^* \hat{A} \psi_3 dx = \int \psi_3^* a_3 \psi_3 dx = a_3 \int \psi_3^* \psi_3 dx = a_3$$

$$\langle a^2 \rangle = \int \psi_3^* \hat{A}^2 \psi_3 dx = \int \psi_3^* a_3 \hat{A} \psi_3 dx = a_3^2 \int \psi_3^* \psi_3 dx = a_3^2$$

$$\sigma_a^2 = \langle a^2 \rangle - \langle a \rangle^2 = a_3^2 - a_3^2 = 0$$

TDSE

Postulate 5

The wavefunction, or state function, of a system evolves in time according to the time-dependent Schrödinger equation

$$\hat{H}\Psi(x, t) = i\hbar \frac{\partial \Psi(x, t)}{\partial t}$$

Derivation of TIDSE For most systems, Hamiltonian does not contain time explicitly, and in those cases we can apply the method of *separation of variables*. $\Psi(x, t) = \psi(x)f(t)$

$$\frac{1}{\psi(x)} \hat{H}\psi(x) = \frac{i\hbar}{f(t)} \frac{df}{dt} = E$$

Then we can separate two equations: $\hat{H}\psi(x) = E\psi(x)$, $\frac{df}{dt} = -\frac{i}{\hbar}Ef(t)$

$$f(t) = e^{-iEt/\hbar} = e^{-i\omega t}, \quad \Psi(x, t) = \psi(x)e^{-i\omega t}$$

$\psi(x)$ are called *stationary state*.

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Hermitian operator

Postulate 2'

To every observable in classical mechanics there corresponds a linear, *Hermitian* operator in quantum mechanics.

The operator \hat{A} is called Hermitian if it satisfies

$$\int f^*(x) \hat{A} g(x) dx = \int g(x) \hat{A}^* f^*(x) dx$$

This condition can be expressed within very compact notation, called *Dirac bracket notation*.

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Dirac notation

Dirac notation gives us vector-like analogy of wavefunctions.

$$\int \psi_1^* \psi_2 dx = \langle \psi_1 | \psi_2 \rangle$$

Properties:

$$\langle \psi_1 | \psi_2 \rangle = \langle \psi_2 | \psi_1 \rangle^*$$

$$\langle \psi_1 | \psi_1 \rangle = 1 \quad \text{for normalized wavefunctions}$$

$$\int \psi_1^* \hat{A} \psi_2 dx = \langle \psi_1 | \hat{A} | \psi_2 \rangle$$

$$\langle \hat{A} \rangle = \langle \psi | \hat{A} | \psi \rangle$$

The two wavefunctions are *orthogonal* to each other if

$$\langle \psi_1 | \psi_2 \rangle = 0$$

$$\begin{aligned} |\psi\rangle &\leftrightarrow \psi(x) \\ \langle\psi| &\leftrightarrow \psi(x)^* \end{aligned}$$

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Hermitian operator

The *Hermitian adjoint* of an operator \hat{A} , \hat{A}^\dagger is

$$\langle \psi_1 | \hat{A} \psi_2 \rangle = \langle \hat{A}^\dagger \psi_1 | \psi_2 \rangle$$

If \hat{A} and \hat{A}^\dagger are same, \hat{A} is called the *Hermitian operator*.

$$\langle \psi_1 | \hat{A} \psi_2 \rangle = \langle \hat{A} \psi_1 | \psi_2 \rangle$$

Hermitian operator has *real* eigenvalue.

$$a \langle f | f \rangle = \langle f | \hat{A} f \rangle = \langle \hat{A} f | f \rangle = a^* \langle f | f \rangle$$



Hermitian operator

Moreover, eigenfunctions of Hermitian operators are orthogonal.

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

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

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

$$0 = (a_n - a_m) \langle \psi_m | \psi_n \rangle$$

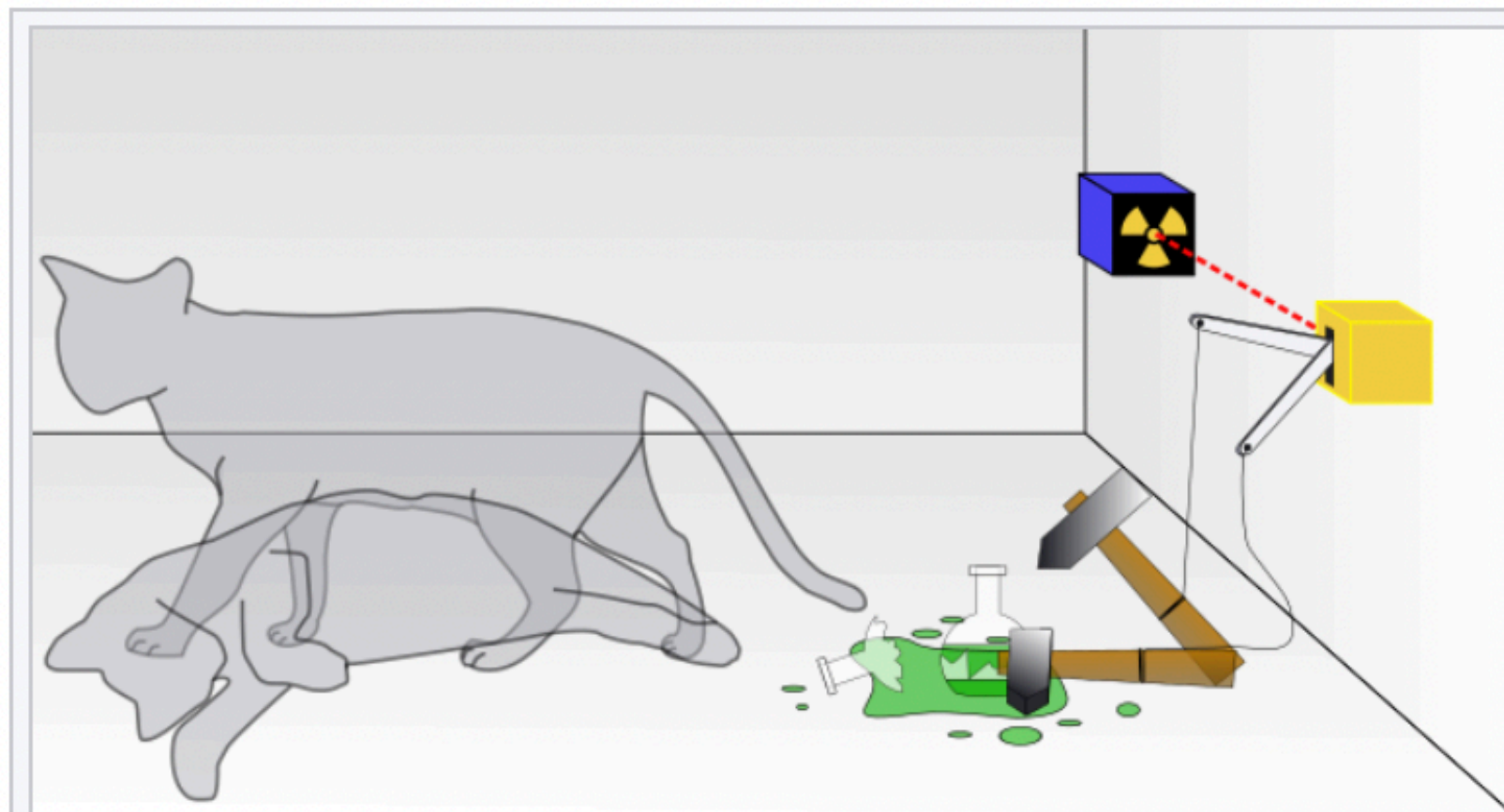
If the eigenvalues are not *degenerate*, then eigenfunctions are orthogonal.

Even if eigenfunctions are degenerate, we can *construct* orthogonal wavefunctions via *Gram-Schmidt orthogonalization*.



Schrödinger's cat

Define *life operator*, which observes the state of a cat inside a box.



Schrödinger's cat: a cat, a flask of poison, and a **radioactive** source are placed in a sealed box. If an internal monitor (e.g. **Geiger counter**) detects radioactivity (i.e. a single atom decaying), the flask is shattered, releasing the poison, which kills the cat. The **Copenhagen interpretation of quantum mechanics** implies that after a while, the cat is *simultaneously alive and dead*. Yet, when one looks in the box, one sees the cat *either alive or dead*, not both alive and dead. This poses the question of when exactly quantum superposition ends and reality resolves into one possibility or the other.

$$\hat{L} | \text{alive} \rangle = + | \text{alive} \rangle$$

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

Before the observation, we don't know the life status of a cat.

Therefore, the cat is under the *superposition status*.

$$| \text{cat} \rangle = \frac{1}{\sqrt{2}} \left(| \text{alive} \rangle + | \text{dead} \rangle \right)$$

However, at the moment of observation (associated with \hat{L}), wavefunction collapse into one of \hat{L} 's eigenstate, alive state or dead state.