Lesson 4: Formalism

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Operator $\hat{O}\, f \;=\; g$ $\quad f, g$ functions

Linear operator $\hat{L}\,(c_1 f_1 \;+\; c_2 f_2) \;=\; c_1 \hat{L} f_1 \;+\; c_2 \hat{L} f_2$

Examples $\hat{O}\, f(x) \;=\; f(x) \;+\; x^2$ no linear

$\hat{O}\, f(x) \;=\; \frac{df(x)}{dx} \;-\; 2f(x)$ linear

$\hat{O}\, f(x) \;=\; \lambda f(x)$ linear

Hermitian or **self-adjoint** linear operator

$$\begin{aligned} \int_{a.s.} d\tau \Psi_1^* \left(\hat{L}\Psi_2\right) &= \left[\int_{a.s.} d\tau \Psi_2^* \left(\hat{L}\Psi_1\right)\right]^* \\ &= \int_{a.s.} d\tau \left(\hat{L}\Psi_1\right)^* \Psi_2 \;\; ; \quad \forall\, \Psi_1,\; \Psi_2 \end{aligned}$$

$\int_{a.s.} d\tau \Psi_1^* \left(\hat{L}\Psi_2\right)$ **matrix element** of $\hat{L}$ between Ψ_1 and Ψ_2 .

Diagonal matrix element if $\Psi_1 \;=\; \Psi_2$ (and equal to the expectation value of $\hat{L}$ in Ψ_1 if it is normalized)

- 1) Linear Hermitian operators have real expectation values
- 2) we call **observables** to physical magnitudes (represented by linear Hermitian operators)

Demonstration 1). Let $\hat{L}$ be a linear Hermitian operator

$$< \hat{L} >_\Psi \;=\; \int_{a.s.} d\tau \Psi^* \left(\hat{L}\Psi\right) \;=\; \left[\int_{a.s.} d\tau \Psi^* \hat{L} \Psi\right]^* \;=\; < \hat{L} >_\Psi^*$$

$\rightarrow < \hat{L} >_\Psi$ is real

- Sum of operators $\hat{C} = \hat{A} + \hat{B} \rightarrow \hat{C}\,\Psi = \hat{A}\,\Psi + \hat{B}\,\Psi$

  If $\hat{A}$ and $\hat{B}$ are Hermitian $\rightarrow$ $\hat{A} + \hat{B}$ is Hermitian
- Product of operators $\hat{C} = \hat{A}\,\hat{B} \rightarrow \hat{C}\,\Psi = \hat{A}\,\hat{B}\,\Psi = \hat{A}\left(\hat{B}\,\Psi\right)$

  In general the product of operators is not commutative
- **Conmutator** of $\hat{A}$ y $\hat{B}$: $[\hat{A},\hat{B}] = \hat{A}\,\hat{B} - \hat{B}\,\hat{A}$

  If $[\hat{A},\hat{B}] = 0 \rightarrow$ $\hat{A}$ and $\hat{B}$ conmute
  - $[\hat{A},\hat{B}] = -\,[\hat{B},\hat{A}]$
  - $[\hat{A} + \hat{B},\hat{C}] = [\hat{A},\hat{C}] + [\hat{B},\hat{C}]$
  - $[\hat{A},\lambda\hat{B}] = \lambda\,[\hat{A},\hat{B}]$; $\lambda \in \mathcal{C}$
  - $[\hat{A},\hat{B}\hat{C}] = \hat{B}[\hat{A},\hat{C}] + [\hat{A},\hat{B}]\hat{C}$

Hermitian conjugate or adjoint operator of $\hat{A}$, $\hat{A}^{\dagger}$

$$\int_{a.s.} d\tau \Phi^* \hat{A}\Psi = \left[\int_{a.s.} d\tau \Psi^* \hat{A}^{\dagger}\Phi\right]^* \quad ; \quad \forall\,\Phi,\,\Psi$$

- If $\hat{A}$ is Hermitian $\hat{A} = \hat{A}^{\dagger}$
- $\left(\hat{A}^{\dagger}\right)^{\dagger} = \hat{A}$
- $\left(\hat{A} + \hat{B}\right)^{\dagger} = \hat{A}^{\dagger} + \hat{B}^{\dagger}$
- $\left(\hat{A}\,\hat{B}\right)^{\dagger} = \hat{B}^{\dagger}\,\hat{A}^{\dagger}$

- $(\lambda)^\dagger = \lambda^*; \quad \lambda \in \mathcal{C}$
- $\left(\lambda \hat{A}\right)^\dagger = \lambda^* \hat{A}^\dagger$; $\lambda \in \mathcal{C}$ (λ is an operator, $\lambda\hat{A}$ operator product)
- If $\hat{A}$ and $\hat{B}$ are Hermitian and $[\hat{A}, \hat{B}] = 0 \quad \rightarrow \hat{A}\,\hat{B}$ is Hermitian
- If $\hat{A}$ is Hermitian so is $\hat{A}^n$
- $\hat{O} = \sum_n c_n \hat{A}^n$; $c_n \in \mathcal{C} \rightarrow \hat{O}^{\,\dagger} = \sum_n c_n^* \left(\hat{A}^n\right)^\dagger$
  - If $\hat{A} = \hat{A}^\dagger \rightarrow \hat{A}^n = \left(\hat{A}^\dagger\right)^n = \left(\hat{A}^n\right)^\dagger \rightarrow$
    $\hat{O}^{\,\dagger} = \sum_n c_n^* \hat{A}^n$
  - If in addition $c_n \in \mathcal{R} \rightarrow \hat{O}^\dagger = \sum_n c_n \hat{A}^n = \hat{O}$

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Eigenfunctions and eigenvalues

- Eigenvalue equation $\hat{O} f_\lambda = e_\lambda\, f_\lambda$; $e_\lambda \in \mathcal{C}$
  f_λ is **eigenfunction** of $\hat{O}$ associated to the **eigenvalue** e_λ
- If more than one f_λ is associated with the same e_λ there is **degeneration**

  e_λ is a $g(\lambda)$ times degenerate eigenvalue if $\exists\, f_{\lambda_1},\ f_{\lambda_2}, \cdots f_{\lambda_{g(\lambda)}}$ linearly independent
  $/\ \hat{O}\, f_{\lambda_i} = e_\lambda\, f_{\lambda_i} \quad ; \quad i = 1, 2 \cdots g(\lambda)$

  $\sum_{i=1}^{g(\lambda)} b_i\, f_{\lambda_i}$ is eigenfunction of $\hat{O}$ associated to e_λ

$$\hat{O}\left(\sum_{i=1}^{g(\lambda)} b_i f_{\lambda_i}\right) = \sum_{i=1}^{g(\lambda)} b_i e_\lambda\, f_{\lambda_i} = e_\lambda \left(\sum_{i=1}^{g(\lambda)} b_i f_{\lambda_i}\right)$$

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- $\hat{O}^n f_\lambda \;=\; e_\lambda^n f_\lambda$
- For a given operator $\;\longrightarrow\;$ solving the eigenvalue equation $\;\Longrightarrow\;$ finding its eigenvalues and eigenfunctions
  Ex. $\quad \hat{H}\;\Psi = \;E\;\Psi$

  $\hat{H} \;=\; \hat{E}_c \;+\; \hat{V} \;=\; i\hbar\frac{\partial}{\partial t}$ operator

  E eigenvalue of $\hat{H}$
  Ψ eigenfunction of $\hat{H}$ (assoc. to E)
- eigenvalues of Hermitian operators are real
  $< \hat{O} >_{f_\lambda} \;=\; \int_{a.s.} d\tau\; {f_\lambda}^* \hat{O}\; f_\lambda \;=\; \int_{a.s.} d\tau\; {f_\lambda}^*\; e_\lambda\; f_\lambda \;=\; e_\lambda \;\longrightarrow$ real
  (expectation value calculated in eigenfunction = eigenvalue)
- **Scalar product** of two functions Φ y Ψ
  $(\Phi,\;\Psi) \;=\; \int_{a.s.}\; d\tau\; \Phi^*\;\Psi$
  $(\Phi,\;\Psi) \;=\; (\Psi,\;\Phi)^*$

Properties of the eigenfunctions

- Eigenfunctions of Hermitian operators associated with different eigenvalues are orthogonal
  $\hat{A}\;\Psi_1 \;=\; a_1\;\Psi_1$ y $\hat{A}\;\Psi_2 \;=\; a_2\;\Psi_2$ con $a_1 \;\neq\; a_2$

$$\int_{a.s.} d\tau\;\Psi_2^*\;\hat{A}\Psi_1 \;=\; a_1 \int_{a.s.} d\tau\;\Psi_2^*\;\Psi_1 \qquad (1)$$

$$\int_{a.s.} d\tau\;\Psi_1^*\;\hat{A}\Psi_2 \;=\; a_2 \int_{a.s.} d\tau\;\Psi_1^*\;\Psi_2 \qquad (2)$$

$\hat{A}$ Hermitian $\;+\;$ (2) $\;\longrightarrow\;$ $\int_{a.s.} d\tau\; \left(\hat{A}\Psi_1\right)^*\;\Psi_2 \;=\; a_2\;\int_{a.s.} d\tau\;\Psi_1^*\;\Psi_2$

$$\text{c.c.} \;\longrightarrow\; \int_{a.s.} d\tau\;\Psi_2^*\left(\hat{A}\Psi_1\right) \;=\; a_2 \int_{a.s.} d\tau\;\Psi_2^*\;\Psi_1 \qquad (3)$$

From (1) $-$ (3) $(a_1 - a_2) \int_{a.s.} d\tau\, \Psi_2^*\, \Psi_1 = 0 \rightarrow \int_{a.s.} d\tau\, \Psi_2^*\, \Psi_1 = (\Psi_2,\, \Psi_1) = 0$

- If there is degeneration $a_1 = a_2$ and methods of ortogonalization must be used (the orthogonality is not guaranteed)
- All linearly independent eigenfunctions of any dynamic variable (= observable $\longrightarrow$ Hermitian operator) span a function space, known as Hilbert space, in the sense that an arbitrary wave function which satisfies the same boundary conditions can be expanded in terms of them

$$\Psi(\vec{r}) = \sum_n c_n\, \phi_n(\vec{r}) \quad ; \quad c_n \in \mathcal{C}$$

$\phi_n(\vec{r})$ set of eigenfunctions of the observable

$$\int_{a.s.} d\tau\, \phi_{n'}^* \Psi(\vec{r}) = \int_{a.s.} d\tau\, \phi_{n'}^* \sum_n c_n\, \phi_n = \sum_n c_n\, \delta_{nn'} = c_{n'}$$

$$\boxed{c_n = \int_{a.s.} d\tau\, \phi_n^* \Psi(\vec{r}) = (\phi_n, \Psi)}$$

(We have assumed that $\int_{a.s.} d\tau\, \phi_{n'}^* \phi_n = \delta_{nn'}\ ;\ \forall n, n'$)

It associates $\Psi \quad \rightarrow \quad |\Psi >$ **ket**

$\Psi^* \quad \rightarrow \quad < \Psi|$ **bra**

$(\Phi,\ \Psi) \quad \rightarrow \quad < \Phi \mid \Psi >$ **bracket**

Therefore $< \Phi| \ \Psi > \ = \ < \Psi| \ \Phi >^*$

Matrix element $\int_{a.s.} d\tau \Phi^* \hat{A} \Psi \ = \ < \Phi|\hat{A}|\Psi > \ = \ < \Phi|\hat{A}\Psi >$

- Adjoint or Hermitian operator of $\hat{A}$ ($\hat{A}^\dagger$)

$$\begin{aligned} < \Psi_1|\hat{A}|\Psi_2 > \ &= \ < \Psi_2|\hat{A}^\dagger|\Psi_1 >^* \\ &= \ < \hat{A}^\dagger \Psi_1|\Psi_2 > \ ; \ \forall \, \Psi_1 \, , \ \Psi_2 \end{aligned}$$

$$\begin{aligned} (\phi,\ a\psi) \ &= \ a\,(\phi,\ \psi) \ \rightarrow \ < \phi \mid a\psi > \ = \ a \ < \phi \mid \psi >; a \in \mathcal{C} \\ (a\,\phi,\ \psi) \ &= \ a^*\,(\phi,\ \psi) \ \rightarrow \ < a\,\phi \mid \psi > \ = \ a^* \ < \phi \mid \psi > \end{aligned}$$

- Eigenvalue eq. (Dirac notation) $\hat{A}\,|a > \ = \ a\,|a >$
- **orthonormality** condition $< \Psi_i \mid \Psi_j > \ = \ \delta_{ij}$
- Eigenfunctions of a Hermitian operator with different eigenvalues are orthogonal

$$\begin{aligned} &\hat{A}\,|a > \ = \ a\,|a > \ ; \ \hat{A}\,|b > \ = \ b\,|b > \\ &< b|\hat{A}\,|a > \ = \ a \ < b|a > \\ &< a|\hat{A}\,|b > \ = \ b \ < a|b > \\ &\qquad\qquad\qquad \Downarrow c.c. \\ &< b|\hat{A}^\dagger\,|a > \ = \ b^* \ < b|a > \end{aligned}$$

but

$$\hat{A} \ = \ \hat{A}^\dagger \ \rightarrow \ a < \ b| \ a > \ = \ b^* \ < b|a > \tag{4}$$

- cont.
  - (I) If $|\, b > \; = \; |\, a > \; \rightarrow \; a \, = \, b \; \rightarrow \; a \, = \, a^* \; \rightarrow$ eigenvalues of Hermitian operators are real
  - (II) from (I)

    (4) $\rightarrow \; a < \, b|\, a > \; = \, b \, < b|a >$

    $\rightarrow \; (a \, - \, b) < \, b|\, a > \; = \, 0$

    $\rightarrow$ if $a \, \neq \, b \; \rightarrow \; < \, b|\, a > \; = \, 0$
- Hermitian operator $\hat{L} \, = \, \hat{L}^\dagger$

$$< \Psi_1|\, \hat{L}|\Psi_2 > \; = \; < \Psi_2|\, \hat{L}|\Psi_1 >^* \; = \; < \hat{L}\, \Psi_1|\Psi_2 > \quad ;$$

$\forall\, \Psi_1 \, , \, \Psi_2$

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Basic Postulates of Quantum Mechanics

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- 1) The quantum state of a system is described by means of a wave function, $\Psi(\vec{r}, t)$ (or ket $|\Psi >$). It contains all the information that can be known about the system. The “solution space” for a given problem is defined to be the set of all **physically acceptable** wave functions for that problem.

- 2) Associated with every measurable quantity A there is some linear, Hermitian operator (**observable**) $\hat{A}$.

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

$$\hat{A}\,\phi_i = a_i\,\phi_i$$

If the system is in an eigenstate of $\hat{A}$ with eigenvalue a_i, then any measurement of the quantity A will yield a_i.

Although measurements must always yield an eigenvalue, **the state does not have to be an eigenstate of $\hat{A}$ initially**. An arbitrary state can be expanded in the **complete set** of eigenfunctions of $\hat{A}$ as

$$\Psi = \sum_i^n c_i\,\phi_i$$

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- 3) (cont.) where n may go to infinity. In this case we only know that the measurement of A will yield one of the values a_i, but we don't know which one.

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- 4) Quantum mechanics is a theory of **probabilities**. Measurements carried out in identical systems described by the same wave function, $\Psi(\vec{r},t)$ do not necessarily yield identical results.
  - 4.1) For

$$\Psi(\vec{r},t) \;=\; \sum_n c_n\,\phi_n \quad ; \quad c_n \;=\; (\phi_n, \Psi)$$

where $\hat{A}\;\phi_n = a_n\,\phi_n$

the probability $P(a_n)$ that a measurement of A will give the **nondegenerate** eigenvalue a_n is

$$P(a_n) \;=\; |\int_{a.s.} d\tau\;\phi_n^*\;\Psi(\vec{r},t)|^2 \;=\; |c_n|^2$$

if $\Psi(\vec{r},t)$ normalized $\;\longrightarrow\;$ $\sum_n |c_n|^2 \;= 1$

and ϕ_n orthonormal basis $\;\longrightarrow\;$ $\int_{a.s.} d\tau\phi_n^*\phi_{n'} \;=\; \delta_{nn'}$

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- 4) (cont.)
  - 4.2) If a_n is **degenerate** and $\Psi(\vec{r},t)$ is **normalized** and ϕ_n^i are a **orthonormal basis**

$$\Psi(\vec{r},t) \;=\; \sum_n \sum_{i=1}^{g_n} c_n^i\;\phi_n^i \quad ; \quad c_n^i \;=\; (\phi_n^i,\;\Psi)$$

where

$$\hat{A}\,\phi_n^i \;=\; a_n\,\phi_n^i \quad ; \quad i \;=\; 1,2,3,\cdots g_n$$

$$P(a_n) \;=\; \sum_{i=1}^{g_n} |\int_{a.s.} d\tau\;(\phi_n^i)^*\;\Psi|^2 \;=\; \sum_{i=1}^{g_n}\;|c_n^i|^2$$

where $\Psi(\vec{r},t)$ normalized $\;\longrightarrow\;$ $\sum_n\;\sum_{i=1}^{g_n} |c_n^i|^2 \;= 1$

orthonormal basis $\;\longrightarrow\;$ $<\phi_n^i|\phi_{n'}^j>=\;\delta_{nn'}\delta_{ij}$

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- 4) (cont.)
  - 4.2) (cont.)

$$\text{from 4)} \quad < \Psi|\hat{A}|\Psi > \; = \; \sum_{nn'} \sum_{ij} \int_{a.s.} d\tau (c_n^i)^* (\phi_n^i)^* \hat{A}\, c_{n'}^j\, \phi_{n'}^j$$

$$= \; \sum_{nn'} \sum_{ij} a_{n'} (c_n^i)^* c_{n'}^j\, \delta_{ij}\, \delta_{nn'} \; = \; \sum_{ni} |c_n^i|^2\, a_n$$

To make sure that, when measuring a magnitude A, we are going to get a certain value, the system has to be in an eigenstate of $\hat{A}$

$$\hat{A}\, \phi_n^i \; = \; a_n\, \phi_n^i \quad ; \quad i \; = \; 1, 2, 3, \cdots g_n \quad ; \quad (\phi_n^i, \phi_n^j) \; = \; \delta_{ij}$$

$$\text{if} \quad \Psi \; = \; \sum_{i=1}^{g_n} c_n^i\, \phi_n^i \quad ; \text{ and } \quad (\Psi, \Psi) \; = \; \sum_{i=1}^{g_n} |c_n^i|^2 \; = \; 1$$

$$\Downarrow$$

$$P_\Psi(a_n) \; = \; 1$$

$$\begin{aligned} (\Psi, \Psi) \quad &= \quad \int_{a.s.} d\tau \Psi^* \Psi \\ &= \quad \int_{a.s.} d\tau \sum_{i=1}^{g_n} \sum_{j=1}^{g_n} c_n^{i*} \phi_n^{i*} c_n^j\, \phi_n^j \\ &= \quad \sum_{i,j=1}^{g_n} c_n^{i*} c_n^j\, \delta_{ij} \; = \; \sum_{i=1}^{g_n} |c_n^i|^2 \end{aligned}$$

- 5) If a measurement of A in state Ψ gives the result a_n, the wavefunction immediately **collapses** into the corresponding eigenstate ϕ_n (in the case that a_n is degenerate, then becomes the projection of Ψ onto the degenerate subspace).

Measurement affects the state of the system

Dirac notation, before measuring

$$|\Psi> \;=\; \sum_k \sum_{i=1}^{g_k} < \phi_k^i|\Psi> \; |\phi_k^i> \;\rightarrow$$

After getting a_n $\rightarrow$ eigenstate

$$\mathcal{N} \sum_{i=1}^{g_n} < \phi_n^i|\Psi> \; |\phi_n^i>$$

- 5) (cont.) If a second measurement of A is performed after the first, the second measurement will give the same result as the first (with unit probability) provided that the second measurement is performed **immediately** after the first.

- 6) The wavefunction of a system evolves in time according to the time-dependent Schrödinger equation

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

(or, in Dirac notation, $i\hbar\frac{\partial|\Psi>}{\partial t} \; = \; \hat{H}|\Psi>$)

The central equation of quantum mechanics must be accepted as a postulate

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Time dependence of the wave function

Time-Dependent Schrödinger Equation, **TDSE** in one dimension

$$i\hbar\frac{\partial\Psi(x,t)}{\partial t} \; = \; \left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} \; + \; \hat{V}(x)\right)\Psi(x,t)$$

We assume $V \; = \; \hat{V}(x)$ (local and time independent)

For this case. Schrödinger eq. can be solved using the method of **separation of variables**
We seek solutions of the type:

$$\Psi(x,t) \; = \; \phi(x)\,T(t)$$

(from them we can build the most general solution)

$$i\hbar\,\phi(x)\frac{dT(t)}{dt} = -\frac{\hbar^2}{2m}T(t)\frac{d^2\phi(x)}{dx^2} + \hat{V}(x)T(t)\phi(x)$$

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$$i\hbar \frac{1}{T} \frac{dT(t)}{dt} \; = \; -\frac{\hbar^2}{2m} \frac{1}{\phi} \frac{d^2\phi(x)}{dx^2} \; + \; \hat{V}(x)$$

The left hand side of the equality is a function only of t, the right one of $x \; \rightarrow \; =$ constant

$$i\hbar \frac{1}{T} \frac{dT(t)}{dt} \; = \; E$$

$$T(t) \; = \; T(0) \; exp(-\frac{iEt}{\hbar})$$

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$$-\frac{\hbar^2}{2m} \frac{1}{\phi} \frac{d^2\phi(x)}{dx^2} \; + \; \hat{V}(x) \; = \; E$$

$$\boxed{-\frac{\hbar^2}{2m} \frac{d^2\phi(x)}{dx^2} + \hat{V}(x)\phi(x) \; = \; E\phi(x)}$$

Time independent Schrödinger equation (TISE)

We will solve it for different potentials $\hat{V}(x)$

$$\Psi(x,t) \; = \; \phi(x) \; exp(-\tfrac{iEt}{\hbar})$$

where $\phi(x)$ is solution of the t independent Schrödinger Eq.

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The solutions are **stationary states** ($\leftrightarrow$ eigenstates of $\hat{H}$)$\rightarrow$ probability density independent on t $\rightarrow$ so does the expected value of any observable independent of t

These states have well-defined energy

$$\hat{H}\Psi(x,t) \;=\; E\Psi(x,t) \;\rightarrow\; <\hat{H}>_\Psi \;=\; E$$

The general solution of Schrödinger Eq. is a linear combination of separable solutions

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By the principle of superposition

If $\Psi(x,0) \;=\; \sum_i \, c_i \, \phi_i(x)$ where

$$\hat{H}\;\phi_i(x) \;=\; E_i\;\phi_i(x)$$

$$\boxed{\Psi(x,t) \;=\; \sum_i \, c_i \, \phi_i(x)\; e^{-\frac{iE_i t}{\hbar}}}$$

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Compatibility of observables

In order to have well-defined eigenvalues of two observables $\hat{A}$ and $\hat{B}$ $\longrightarrow$ simultaneous eigenstate of both

$\hat{A}$ and $\hat{B}$ **compatible** (=**simultaneous measurable**) = eigenvalues of both can be assigned simultaneously to every eigenfunction $\longrightarrow$ there is a complete set of common eigenfunctions

$$\hat{B}\times \qquad [\ \hat{A}\,\Psi_{a_n b_{n'}} = a_n\,\Psi_{a_n b_{n'}}]$$
$$\hat{A}\times \qquad [\ \hat{B}\,\Psi_{a_n b_{n'}} = b_{n'}\,\Psi_{a_n b_{n'}}]$$
$$\left(\hat{A}\hat{B}-\hat{B}\hat{A}\right)\Psi_{a_n b_{n'}} = 0 \rightarrow \left[\hat{A},\hat{B}\right] = 0\,;\ (\forall\,\Psi_{a_n b_{n'}})$$

- Condition for two observables to be measured simultaneously

  $\left[\hat{A},\hat{B}\right] = 0$

- If $\left[\hat{A},\hat{B}\right] = 0$ there is a common set of eigenfunctions

  Let Ψ_b / $\hat{B}\Psi_b = b\,\Psi_b$ with nondegenerate b

$$\hat{A}\hat{B}\Psi_b = \hat{B}(\hat{A}\Psi_b) = b(\hat{A}\Psi_b) \longrightarrow \hat{A}\Psi_b = a\,\Psi_b$$

  (because b is nondegenerate)

  Ψ_b eigenfunction of $\hat{B}$ $\longrightarrow$ eigenfunction of $\hat{A}$

  One can also get a common eigenbasis of $\hat{A}$ and $\hat{B}$ for degenerate eigenvalues when $\left[\hat{A},\hat{B}\right] = 0$ (we will not study how to get it).

The expected value of an operator $\hat{O}$ in a normalized state Ψ is

$$< \hat{O} >_\Psi \; = \bar{\hat{O}}_\Psi \; = \int_{a.s.} d\tau \Psi^* \hat{O} \Psi \; = \; < \Psi | \hat{O} | \Psi >$$

Ψ and $\hat{O}$ in general also depend on time $t \;\rightarrow\; < \hat{O} >_\Psi$.

$< \hat{O} >_\Psi$ only depends on t

$$\frac{\partial\, \bar{\hat{O}}}{\partial t} \; = \; \frac{d\, \bar{\hat{O}}}{dt} \; = \; \int_{a.s.} d\tau \Psi^* \frac{\partial \hat{O}}{\partial t} \Psi \; + \; \int_{a.s.} d\tau \left(\frac{\partial \Psi^*}{\partial t} \hat{O} \Psi \; + \; \Psi^* \hat{O} \frac{\partial \Psi}{\partial t} \right)$$

TDSE $\quad i\hbar \frac{\partial \Psi}{\partial t} \; = \; \hat{H} \Psi$

$$\frac{\partial \Psi}{\partial t} \; = \; -\frac{i}{\hbar} \hat{H} \Psi \quad \rightarrow \quad \left(\frac{\partial \Psi}{\partial t} \right)^* \; = \; \frac{\partial \Psi^*}{\partial t} \; = \; \frac{i}{\hbar} \left(\hat{H} \Psi \right)^*$$

Therefore

$$\frac{d\, \bar{\hat{O}}}{dt} \; = \; \int_{a.s.} d\tau \Psi^* \frac{\partial \hat{O}}{\partial t} \Psi \; + \; \frac{i}{\hbar} \int_{a.s.} d\tau \left[\left(\hat{H}\; \Psi \right)^* \hat{O}\; \Psi \; - \; \Psi^* \hat{O}\; \hat{H}\; \Psi \right]$$

$\hat{H}$ is Hermitian $\;\rightarrow\; \int_{a.s.} d\tau \left(\hat{H}\; \Psi \right)^* \; \Phi \; = \; \int_{a.s.} d\tau \Psi^* \hat{H} \Phi$

taking $\Phi \; = \; \hat{O}\Psi \;\; \rightarrow \;\; \int_{a.s.} d\tau \left(\hat{H}\; \Psi \right)^* \hat{O}\; \Psi \; = \; \int_{a.s.} d\tau \Psi^* \hat{H} \hat{O} \Psi$ (because $\hat{H}$ is Hermitian)

$$\begin{aligned} \frac{d\, \bar{\hat{O}}}{dt} \; &= \; \int_{a.s.} d\tau \Psi^* \frac{\partial \hat{O}}{\partial t} \Psi \; + \; \frac{i}{\hbar} \int_{a.s.} d\tau \left[\Psi^* \hat{H}\; \hat{O}\; \Psi \; - \; \Psi^* \hat{O}\; \hat{H}\; \Psi \right] \\ &= \; \int_{a.s.} d\tau \Psi^* \frac{\partial \hat{O}}{\partial t} \Psi \; + \; \frac{i}{\hbar} \int d\tau \Psi^* \left[\hat{H} \,, \hat{O} \right] \; \Psi \end{aligned}$$

Time evolution of the mean value of an operator $\hat{O}$

$$\boxed{\frac{d <\hat{O}>_\Psi}{dt} \ = \ < \frac{\partial \hat{O}}{\partial t} >_\Psi \ + \ \frac{i}{\hbar} \ < [\hat{H} \ , \hat{O}] >_\Psi}$$

Ehrenfest's Theorem

Calculation of basic conmutators

$$\begin{aligned}
[\hat{x}, \hat{p}_x] \ \Psi &= [\hat{x}, -i\hbar \frac{\partial}{\partial x}] \Psi \\
&= -i\hbar \hat{x} \frac{\partial \Psi}{\partial x} \ + \ i\hbar \frac{\partial (\hat{x}\Psi)}{\partial x} \\
&= -i\hbar \hat{x} \frac{\partial \Psi}{\partial x} \ + \ i\hbar \Psi \ + \ i\hbar \hat{x} \frac{\partial \Psi}{\partial x} \\
&= i\hbar \Psi
\end{aligned}$$

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

$$[\hat{x},\hat{x}] \;=\; [\hat{x},\hat{y}] \;=\; [\hat{x},\hat{z}] \;=\; 0$$

$$[\hat{x},\hat{p}_y] \;=\; [\hat{x},\hat{p}_z] \;=\; 0$$

$$\boxed{\begin{aligned}[\hat{x}_i,\hat{x}_j] \;&=\; 0\\ [\hat{x}_i,\hat{p}_j] \;&=\; i\hbar\delta_{ij}\\ [\hat{p}_i,\hat{p}_j] \;&=\; 0\end{aligned}}$$

Calculation of $[\hat{V},\hat{p}_x]$

$$\begin{aligned}[\hat{V},\hat{p}_x]\Psi \quad &= \quad -i\hbar[\hat{V},\frac{\partial}{\partial x}]\Psi\\ &= \quad -i\hbar\hat{V}\frac{\partial \Psi}{\partial x} \;+i\hbar\frac{\partial\left(\hat{V}\Psi\right)}{\partial x}\\ &= \quad -i\hbar\hat{V}\frac{\partial \Psi}{\partial x} \;+i\hbar\frac{\partial \hat{V}}{\partial x}\;\Psi \;+\; i\hbar\hat{V}\frac{\partial \Psi}{\partial x}\\ &= \quad i\hbar\frac{\partial \hat{V}}{\partial x}\;\Psi\end{aligned}$$

$$\boxed{[\hat{V},\hat{p}_x] \;=\; i\hbar\tfrac{\partial \hat{V}}{\partial x}}$$

We will see how average values of $\hat{O} = \hat{x}, \hat{p}_x$ evolve over time

$\hat{x}, \hat{p}_x$ as quantum operators do not depend explicitly on t, so

$$\frac{d < \hat{x} >}{dt} = \frac{i}{\hbar} < [\hat{H}, \hat{x}] > \quad ; \quad \frac{d < \hat{p}_x >}{dt} = \frac{i}{\hbar} < [\hat{H}, \hat{p}_x] >$$

If

$$\hat{H} = \frac{1}{2m}\left(\hat{p}_x^2 + \hat{p}_y^2 + \hat{p}_z^2\right) + \hat{V}(x, y, z)$$

- $[\hat{H}, \hat{x}] = \frac{1}{2m}[\hat{p}_x^2, \hat{x}] = \frac{1}{2m}\{\hat{p}_x[\hat{p}_x, \hat{x}] + [\hat{p}_x, \hat{x}]\hat{p}_x\}$

$$= \frac{1}{2m}\{-2i\hbar\hat{p}_x\} = \frac{\hbar}{im}\hat{p}_x$$

- $[\hat{H}, \hat{p}_x] = \left[\hat{V}(x, y, z), \hat{p}_x\right] = i\hbar\frac{\partial\hat{V}}{\partial x}$

$$\frac{d < \hat{x} >}{dt} = \frac{< \hat{p}_x >}{m} \quad ; \quad \frac{d < \hat{p}_x >}{dt} = -\left\langle \frac{\partial\hat{V}}{\partial x} \right\rangle$$

In three dimensions, **Ehrenfest's Theorem**

$$\boxed{\frac{d<\hat{\vec{r}}>}{dt} = \frac{<\hat{\vec{p}}>}{m} \quad ; \quad \frac{d<\hat{\vec{p}}>}{dt} = -\left\langle \vec{\nabla}\hat{V} \right\rangle}$$

Classical equations of Hamilton-Jacobi

$$\frac{d\vec{r}}{dt} = \frac{\vec{p}}{m} \quad ; \quad \frac{d\vec{p}}{dt} = -\vec{\nabla}V$$

- Quantum equations are similar to the classical ones
- Calculation of the classical ones at $<\vec{r}>$ and $<\vec{p}>$ match the quantum ones in cases where

$$\frac{\partial V}{\partial x}|_{\bar{x}} = \left\langle \frac{\partial \hat{V}}{\partial x} \right\rangle$$

  Not always the case

  In general $\Rightarrow$ force estimated at $<\vec{r}> \neq$ expected value of the force
- In general $<\vec{r}>$ and $<\vec{p}>$ do not obey the classical equations

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Constants of the motion and conservation laws

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An observable $\hat{A}$ is a **constant of motion** if

$$\frac{\partial \hat{A}}{\partial t} = 0 \quad y \quad [\hat{A}, \hat{H}] = 0$$

- If $\hat{A}$ is a confstant of motion $\frac{d<\hat{A}>_\Psi}{dt} = 0$
  $<\hat{A}>_\Psi$ does not vary over time in any state, $<\hat{A}>_\Psi$ is conserved
- If $\hat{H} \neq \hat{H}(t) \rightarrow <\hat{H}>_\Psi$ is constant $\rightarrow$ energy is conserved (conservative system)
- If $\frac{\partial \hat{V}}{\partial x} = 0$ (the force F_x is zero)

  $\rightarrow [\hat{H}, \hat{p}_x] = i\hbar \frac{\partial \hat{V}}{\partial x} = 0 \rightarrow$ is conserved $<\hat{p}_x>_\Psi \rightarrow \hat{p}_x$ is a constant of motion

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- If $\vec{\bigtriangledown}\hat{V} \;=\; 0 \;\;\rightarrow\;\; <\hat{\vec{p}}>_\Psi \;\;=$ is constant $\;\;\rightarrow\;\;$ is conserved
- Central forces $\hat{V} \;=\; \hat{V}(r)$ (spherical coordinates)

$$\hat{L}_x \;=\; i\hbar\left(\sin\phi\frac{\partial}{\partial\theta} \;+\; \cot\theta\cos\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_y \;=\; i\hbar\left(-\cos\phi\frac{\partial}{\partial\theta} \;+\; \cot\theta\sin\phi\frac{\partial}{\partial\phi}\right)$$

$$\hat{L}_z \;=\; -\,i\hbar\frac{\partial}{\partial\phi}$$

$$[\hat{L}_i, \hat{L}_j] \;\;=\;\; i\hbar\epsilon_{ijk}\hat{L}_k \qquad (5)$$

$$\hat{L}^2 \;=\; -\,\hbar^2\left(\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2} \;+\; \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)\right)$$

$$\hat{L}^2 \;=\; \hat{L}^2(\theta,\phi) \;\;;\;\; \hat{\vec{L}} \;=\; \hat{\vec{L}}(\theta,\phi)$$

$$\hat{H}_0 \;=\; \hat{T} \;+\; \hat{V}(r) \;=\; \hat{T}_r \;+\; \frac{\hat{L}^2}{2mr^2} \;+\; \hat{V}(r)$$

(spherical coordinates)

$[\hat{L}^2, \hat{V}(r)] \;=\; 0 \;\;;\;\; [\hat{H}_0, \hat{L}^2] \;=\; 0 \;\;\rightarrow$

$< \hat{L}^2 >_\Psi$ independent on t, it is conserved

$$[\hat{L}^2, \hat{\vec{L}}] \quad = \quad 0 \tag{6}$$

$\rightarrow \ [\hat{H}_0, \hat{\vec{L}}] \ = \ 0 \ \rightarrow \ \ < \hat{\vec{L}} >_\Psi$ independent on t, it is conserved

$\hat{L}^2$, $\hat{\vec{L}}$ are constants of motion if $\hat{V} \ = \ \hat{V}(r)$

- If $\hat{H}_1 \ = \ \hat{H}_0 \ + \ \alpha \, \hat{L}_z$ (magnetic field with direction z)
  - $[\hat{H}_1, \hat{L}_z] \ = \ 0 \ \ \rightarrow \ \ < \hat{L}_z >_\Psi \ = \ $ cte.
  - $[\hat{H}_1, \hat{L}_x] \ = \ i\hbar\alpha\hat{L}_y \ \neq 0$
  - $[\hat{H}_1, \hat{L}_y] \ = \ - i\hbar\alpha\hat{L}_x \ \neq 0$

  $\hat{L}_x$ y $\hat{L}_y$ are not constants of motion for $\hat{H}_1$
  for this case $< \hat{L}_x >_\Psi$ and $< \hat{L}_y >_\Psi$ depend on t for any state

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Demonstration of (5)

$$\begin{aligned}
[\hat{L}_x, \hat{L}_y] &= [y\,p_z - z\,p_y, z\,p_x - x\,p_z] \\
&= [y\,p_z, z\,p_x] \ + \ [z\,p_y, x\,p_z] \\
&= y\,[p_z, z]\,p_x \ + \ x\,[z, p_z]\,p_y \\
&= \ - i\hbar y\,p_x \ + \ i\hbar x\,p_y \ = \ i\hbar\hat{L}_z
\end{aligned}$$

analogously $[\hat{L}_i, \hat{L}_j] \ = \ i\hbar\epsilon_{ijk}\hat{L}_k \quad (\sum_k \ \rightarrow$ repeated index$)$

$$\text{Levy-Civita tensor } \epsilon_{ijk} = \begin{cases} 0 & \text{if any index is repeated} \\ 1 & \text{if ijk is cyclic permutation of 123} \\ -1 & \text{if ijk is non-cyclic permutation of 123} \end{cases}$$

$i = 1 \ \rightarrow \ x \ \ ; \ \ i = 2 \ \rightarrow \ y \ \ ; \ \ i = 3 \ \rightarrow \ z$

Cyclic permutations: (123) (231) (312)

Non-cyclic permutations: (132) (213) (321)

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Demonstration of (6)

$$\begin{aligned}
[\hat{L}^2, \hat{L}_x] &= [\hat{L}_x^2 + \hat{L}_y^2 + \hat{L}_z^2, \hat{L}_x] = [\hat{L}_y^2, \hat{L}_x] + [\hat{L}_z^2, \hat{L}_x] \\
&= \hat{L}_y [\hat{L}_y, \hat{L}_x] + [\hat{L}_y, \hat{L}_x] \hat{L}_y + \hat{L}_z [\hat{L}_z, \hat{L}_x] + [\hat{L}_z, \hat{L}_x] \hat{L}_z \\
&= -i\hbar \hat{L}_y \hat{L}_z - i\hbar \hat{L}_z \hat{L}_y + i\hbar \hat{L}_z \hat{L}_y + i\hbar \hat{L}_y \hat{L}_z = 0
\end{aligned}$$

analogously $[\hat{L}^2, \hat{L}_y] = [\hat{L}^2, \hat{L}_z] = 0$

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