

## Chapter 7. Theorems and Postulates of Quantum Mechanics

Theorem: a true statement that can be proven.

Postulate: a statement that is assumed true without proof.

### Theorems:

1. The eigenvalues of a Hermitian operator are real numbers.

An operator A is said to be Hermitian if:  $\langle A \rangle = \langle A \rangle^* \Rightarrow \int \psi^* \hat{A} \psi d\tau = \int \psi \left( \hat{A} \psi \right)^* d\tau$

Or, for two different functions:  $\int G^* \hat{A} F d\tau = \int F \left( \hat{A} G \right)^* d\tau$

**Proof:** we need to prove that  $a = a^*$   $\int \psi^* \hat{A} \psi d\tau = \int \psi \left( \hat{A} \psi \right)^* d\tau$

$$\int \psi^* \cdot a \cdot \psi d\tau = \int \psi \cdot a^* \cdot \psi^* d\tau$$

$$(a - a^*) \int |\psi|^2 d\tau = 0$$

$$a - a^* = 0$$

$$a = a^*$$

Examples of Hermitian operators:

1. One-particle, 1D potential energy operator:  $\hat{V}(x) = V(x)$ .

$$\langle V(x) \rangle = \langle V(x) \rangle^*$$

$$\langle V(x) \rangle = \int \psi^* \hat{V} \psi dx = \int \psi^* V \psi dx$$

$$\langle V(x) \rangle^* = \int \psi \left( \hat{A} \psi \right)^* dx = \int \psi V^* \psi^* dx = \int \psi^* V \psi dx$$

↑  
since V is a real number

2. Two eigenfunctions of a Hermitian operator B that correspond to different eigenvalues are orthogonal. Eigenfunctions of B that belong to a degenerate eigenvalue can be chosen to be orthogonal.

Two functions are orthogonal if:  $\int f_1^* f_2 d\tau = 0$

**Proof:** For two functions F and G:  $\left. \begin{array}{l} \hat{B} F = sF \\ \hat{B} G = tG \end{array} \right\}$  We want to prove that:  $\int F^* G d\tau = 0$

$$\int F^* \hat{B} G d\tau = \int G \left( \hat{B} F \right)^* d\tau \longrightarrow \text{Hermitian nature of B operator}$$

$$\int F^* t G d\tau = \int G (s F)^* d\tau \longrightarrow \text{Theorem 1}$$

$$t \int F^* G d\tau = s^* \int G F^* d\tau = s \int G F^* d\tau$$

$$(t - s) \int G F^* d\tau = 0$$

**If  $s \neq t$ :**  $\int G F^* d\tau = 0$

**If  $s = t$ :** We can choose G and F to be orthogonal.

$$\left. \begin{array}{l} \hat{B} F = s F \\ \hat{B} G = s G \end{array} \right\} \text{We can choose } g_1 \text{ and } g_2: \begin{array}{l} g_1 = F \\ g_2 = G + cF \end{array} \longrightarrow \text{Orthogonality constant}$$

$$\int g_1^* g_2 d\tau = 0$$

$$\int F^* (G + cF) d\tau = \int F^* G d\tau + c \int F^* F d\tau = 0$$

$$c = - \frac{\int F^* G d\tau}{\int F^* F d\tau}$$

*Although there is no guarantee that the eigenfunctions of a degenerate eigenvalue are orthogonal, we can always choose them to be orthogonal.*

3. Let the functions  $g_1, g_2, \dots$  be the complete set of eigenfunctions of the Hermitian operator  $A$  and let the function  $F$  be an eigenfunction of operator  $A$  with eigenvalue  $k$ ; then if  $F$  is expanded as  $F = \sum a_i g_i$ , the only nonzero coefficients  $a_i$  are those for which  $g_i$  has the eigenvalue  $k$ .

-We showed in Chapter 4 that Taylor series can be used to expand a function as a linear combination of powers of  $(x-a)$ . We can also use other functions for expansion. For example: sine and cosine in Fourier series. We can also expand a function using eigenfunctions of a certain Hermitian operator.


-Complete set: if any function  $f$  can be expanded using that set of functions.

-Theorem 3 states the following:

$$\hat{A} F = kF$$

$$F = \sum a_i g_i$$

$g_1, g_2, g_3, \dots$  represent a complete set of eigenfunctions of operator  $A$ .

  $a_i$  will be nonzero only if:  $\hat{A} g_i = k g_i$

**Proof:**  $F = \sum a_i g_i \quad / \cdot g_k^*$

$$g_k^* F = \sum a_i g_i g_k^*$$

$$\int g_k^* F d\tau = \int \sum a_i g_i g_k^* d\tau = \sum a_i \int g_i g_k^* d\tau = a_k$$



use orthonormality

If  $F$  and  $g_k$  correspond to different eigenvalues, they will be orthogonal and  $a_k$  will vanish.

4. If the linear operators  $A$  and  $B$  have a common complete set of eigenfunctions, then  $A$  and  $B$  commute.

**Proof:**

$$\hat{A} g_i = a_i g_i$$

$$\hat{B} g_i = b_i g_i$$

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

We begin by  
expanding  $f$ :

$$\left( \hat{A} \hat{B} - \hat{B} \hat{A} \right) f = \sum c_i \left( \hat{A} \hat{B} - \hat{B} \hat{A} \right) g_i$$

$$= \sum c_i \left[ \hat{A} \left( \hat{B} g_i \right) - \hat{B} \left( \hat{A} g_i \right) \right]$$

$$= \sum c_i \left[ \hat{A} (b_i g_i) - \hat{B} (a_i g_i) \right]$$

$$= \sum c_i [a_i b_i g_i - b_i a_i g_i] = 0$$

5. If the Herminian operators A and B commute, we can select a common complete set of eigenfunctions for them.

$$\text{If: } \hat{A} g_i = a_i g_i \implies \hat{B} g_i = b_i g_i$$

**Proof:**

$$\hat{A} g_i = a_i g_i \quad \text{Operate on both sides by operator B}$$

$$\begin{aligned} \hat{B} \hat{A} g_i &= \hat{B}(a_i g_i) \\ \hat{A} \hat{B} g_i &= a_i (\hat{B} g_i) \end{aligned}$$

Since operators A and B commute and since operator B is linear

- Function  $Bg_i$  is eigenfunction of operator A with eigenvalue  $a_i$ . If eigenvalues of operator A are nondegenerate, then  $g_i$  and  $Bg_i$  must be linearly dependent (one function must be a multiple of another):

$$\hat{B} g_i = b_i g_i$$

6. If  $g_i$  and  $g_j$  are eigenfunctions of the Hermitian operator  $A$  with different eigenvalues and if operator  $B$  is a linear operator that commutes with operator  $A$ , then:

$$\int g_j^* \hat{B} g_i d\tau = 0 \quad \text{for } a_j \neq a_i$$


**Proof:**

$$\left. \begin{array}{l} \hat{A} g_i = a_i g_i \\ \hat{A} g_j = a_j g_j \end{array} \right\} \int g_j^* \hat{B} g_i d\tau = 0$$

-  $g_i$  is also an eigenfunction of operator  $B$  (Theorem 5)

$$\hat{B} g_i = b_i g_i$$

$$\int g_j^* \hat{B} g_i d\tau = b \int g_j^* g_i d\tau = 0$$

 since functions are orthogonal (theorem 2)

7. When the potential energy  $V$  is an even function, we can choose the stationary state wave functions so that each  $\Psi_i$  is either an even function or an odd function.

Even functions:  $f(x)=f(-x)$

Odd functions:  $f(x)=-f(-x)$

Parity operator:  $\hat{\Pi} f(x, y, z) = f(-x, -y, -z)$

The eigenvalues of the parity operator:

$$\hat{\Pi} g_i = c_i g_i$$

$$\hat{\Pi}^2 f(x, y, z) = \hat{\Pi} \left[ \hat{\Pi} f(x, y, z) \right] = \hat{\Pi} (f(-x, -y, -z)) = \hat{1} f(x, y, z)$$

$$\hat{\Pi}^2 = \hat{1}$$

$$\hat{\Pi}^2 g_i = c_i^2 g_i \rightarrow c_i^2 = 1 \rightarrow c_i = \pm 1$$

If  $c_i = +1$ :  $g_i$  is an even function  
 If  $c_i = -1$ :  $g_i$  is an odd function

$$\text{If } \left[ \hat{H}, \hat{\Pi} \right] = 0$$

Then, we can choose the wavefunctions so that they are either even or odd

**Proof:**

$$\left[ \hat{H}, \hat{\Pi} \right] = \left[ \hat{T}, \hat{\Pi} \right] + \left[ \hat{V}, \hat{\Pi} \right] = \left( -\frac{\hbar^2}{2m} \left( \left[ \frac{\partial^2}{\partial x^2}, \hat{\Pi} \right] + \left[ \frac{\partial^2}{\partial y^2}, \hat{\Pi} \right] + \left[ \frac{\partial^2}{\partial z^2}, \hat{\Pi} \right] \right) \right) + \left[ \hat{V}, \hat{\Pi} \right]$$

$$\left[ \frac{\partial^2}{\partial x^2}, \hat{\Pi} \right] = 0 \xrightarrow{\text{Since}} \hat{\Pi} \left[ \frac{\partial^2}{\partial x^2} f(x, y, z) \right] = \frac{\partial}{\partial(-x)} \frac{\partial}{\partial(-x)} f(-x, -y, -z) = \frac{\partial^2}{\partial x^2} f(-x, -y, -z) = \frac{\partial^2}{\partial x^2} \hat{\Pi} f(x, y, z)$$

Similar holds for y and z coordinates. Thus:  $\left[ \hat{H}, \hat{\Pi} \right] = \left[ \hat{V}, \hat{\Pi} \right]$

$$\hat{\Pi} \hat{V} f(x, y, z) = \hat{\Pi} (V(x, y, z) f(x, y, z)) = V(-x, -y, -z) f(-x, -y, -z)$$

If V is an even function:  $V(-x, -y, -z) = V(x, y, z)$

$$\hat{\Pi} \hat{V} f(x, y, z) = V(x, y, z) f(-x, -y, -z) = \hat{V} \hat{\Pi} f(x, y, z)$$

Parity helps in evaluation of integrals:  $\int_{-\infty}^{\infty} f_x^{ODD} dx = 0$

$$\int_{-\infty}^{\infty} f_x^{EVEN} dx = 2 \int_0^{\infty} f_x^{EVEN} dx$$

8. If  $b_m$  is a nondegenerate eigenvalue of the operator  $B$  and  $g_m$  is the corresponding normalized wavefunction, then when the property  $B$  is measured in a quantum mechanical system whose state function at the time of the measurement is  $\Psi$ , the probability of getting the result  $b_m$  is given by  $|c_m|^2$ , where  $c_m$  is the coefficient of  $g_m$  in the expansion  $\Psi = \sum c_i g_i$ . If the eigenvalue  $b_m$  is degenerate, the probability of obtaining  $b_m$  when  $B$  is measured is found by adding  $|c_i|^2$  values for these eigenfunctions whose eigenvalue is  $b_m$ .

$$\hat{B} g_i = b_i g_i$$

$b_i$  are the only possible outcomes of a measurement

Since  $g_i$  's form a complete set, we can use them to expand  $\Psi$

$$\Psi = \sum c_i g_i$$

Normalization condition

$$\int \Psi^* \Psi d\tau = 1 = \int \sum_i \sum_k c_i^* c_k g_i^* g_k d\tau = \sum_i \sum_k c_i^* c_k \int g_i^* g_k d\tau$$

$g_i$  and  $g_k$  are orthonormal

$$\sum_i \sum_k c_i^* c_k \int g_i^* g_k d\tau = \sum_i \sum_k c_i^* c_k \delta_{ik} \Rightarrow \sum_i |c_i|^2 = 1$$

The average value of a property:

$$\langle B \rangle = \int \Psi^* \hat{B} \Psi d\tau = \sum_i \sum_j c_i^* c_j \int g_i^* \hat{B} g_j d\tau = \sum_i \sum_j c_i^* c_j b_j \int g_i^* g_j d\tau$$

$$\langle B \rangle = \sum_i |c_i|^2 b_i$$

In general, an average value of a certain observable will be an average of N measurement outcomes:

Instead of summing all observed values, we can sum all possible outcomes and multiply each possible value by the number of times it was observed.

$$\langle B \rangle = \frac{\sum_{j=1}^N b_j}{N} \longrightarrow \langle B \rangle = \frac{\sum_b n_b b}{N} = \sum_b \frac{n_b}{N} b = \sum_b P_b \cdot b$$

From the two equations above, we can conclude that:

$$P_{bi} = |c_i|^2$$

The result of a measurement can be predicted with certainty only if the wavefunction  $\Psi$  is one of the eigenfunctions  $g$ . If the wavefunction  $\Psi$  is expressed as an expansion of eigenfunctions  $g$ , then  $c^2$  represents a probability that the given eigenvalue will be obtained in a measurement.

9. If the property B is measured in a quantum mechanical system whose state function is  $\Psi$ , then the probability of observing the eigenvalue  $b_j$  is:

$$\left| \int g_j^* \Psi d\tau \right|^2$$

Where  $g_j$  is the eigenfunction corresponding to the eigenvalue  $b_j$ .

**Proof:** 
$$\int g_j^* \Psi d\tau = \sum_i c_i \int g_j^* g_i d\tau = \sum_i c_i \delta_{ij} = c_j$$

$$|c_j|^2 = \left| \int g_j^* \Psi d\tau \right|^2$$

Example: Suppose that a particle in a box of length  $l$  is in the nonstationary state:

$$\Psi = \sqrt{\frac{105}{l^7}} \cdot x^2(l-x) \quad \text{for } 0 \leq x \leq l$$

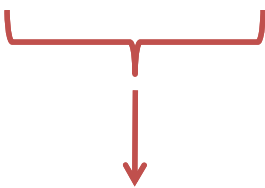
Give the possible outcomes of the energy measurement and their probabilities.

Possible outcomes:  $E = \frac{n^2 h^2}{8ml^2}$

Probabilities:  $|c_n|^2 = \left| \int g_j^* \Psi d\tau \right|^2$  where:  $g_j = \sqrt{\frac{2}{l}} \cdot \sin \frac{n\pi x}{l}$

$$|c_n|^2 = \left| \int_0^l \sqrt{\frac{2}{l}} \sin\left(\frac{n\pi x}{l}\right) \cdot \sqrt{\frac{105}{l^7}} x^2(l-x) dx \right|^2 = \frac{210}{l^8} \left| \int_0^l \sin\left(\frac{n\pi x}{l}\right) (x^2 l - x^3) dx \right|^2$$

$$= \frac{210}{l^8} \left| \int_0^l l x^2 \sin\left(\frac{n\pi x}{l}\right) dx - \int_0^l x^3 \sin\left(\frac{n\pi x}{l}\right) dx \right|^2$$



$$\int x^2 \sin(bx) dx \rightarrow$$

$$\int u dv = uv - \int v du$$

$$u = x^2$$

$$du = 2x dx$$

$$dv = \sin(bx) dx$$

$$v = -\frac{1}{b} \cos(bx) dx$$

$$\int u dv = uv - \int v du$$

$$u = 2x$$

$$du = 2 dx$$

$$dv = \cos(bx) dx$$

$$v = \frac{1}{b} \sin(bx) dx$$

$$\int x^2 \sin(bx) dx = x^2 \left( -\frac{1}{b} \right) \cos(bx) + \frac{1}{b} \int \cos(bx) 2x dx$$

$$\begin{aligned}
\int x^2 \sin(bx) dx &= x^2 \left( -\frac{1}{b} \right) \cos(bx) + \frac{1}{b} \left( 2x \frac{1}{b} \sin(bx) - \int \frac{1}{b} \sin(bx) 2 dx \right) \\
&= -\frac{x^2}{b} \cos(bx) + \frac{1}{b} \left( \frac{2x}{b} \sin(bx) + \frac{2}{b} \frac{1}{b} \cos(bx) \right) \\
&= \frac{2x}{b^2} \sin(bx) + \left( \frac{2}{b^3} - \frac{x^2}{b} \right) \cos(bx)
\end{aligned}$$

Similarly:  $\int x^3 \sin(bx) dx = \left( \frac{3x}{b^2} - \frac{6}{b^4} \right) \sin(bx) + \left( \frac{6x}{b^3} - \frac{x^3}{b} \right) \cos(bx)$

Since  $\sin(n\pi)=0$ , sine terms do not contribute. The probability will be:

$$\frac{840}{n^6 \pi^6} \left[ 5 + 4(-1)^n \right]$$

For n=1	P=0.87
n=2	P=0.123
n=3	P=0.0012

## Postulates of Quantum Mechanics

The formalism of quantum mechanics is based on a number of postulates. These postulates cannot be derived, but are based on a wide range of experimental observations. They represent the minimal set of assumptions needed to develop the theory of quantum mechanics.

1. The state of a system is described by a function  $\Psi$  of the coordinates and time. This function, called the state function or wave function, contains all the information that can be determined about the system. We further postulate that  $\Psi$  is single-valued, continuous and quadratically integrable. For continuum states, the quadratic integrability requirement is omitted.

2. To every physically observable property there corresponds a linear Hermitian operator. To find this operator, we write down the classical-mechanical expression for the observable and then replace each coordinate by operator  $x$  and each momentum by:  $-i\hbar \frac{\partial}{\partial x}$

- Operator must be Hermitian, since observable must be a real number.
- Operator must be linear in order to achieve superposition of states.

3. The only possible values that can result from measurement of the physically observable property B are the eigenvalues  $b_i$  in the equation:

$$\hat{B} g_i = b_i g_i$$

where operator B corresponds to the property B. The eigenfunctions  $g_i$  are required to be well-behaved.

4. If operator B is any linear Hermitian operator that represents a physically observable property, then the eigenfunctions  $g_i$  of operator B form a complete set.

This allows us to expand the wavefunction for any state as a superposition of the orthonormal eigenfunctions of any quantum-mechanical operator:

$$\Psi = \sum_i c_i g_i$$

5. The average value of a physical observable at time t is:  $\langle B \rangle = \int \Psi^* \hat{B} \Psi d\tau$

The probability of observing a certain value  $b_i$  is:  $P_{bi} = \int g_i^* \Psi d\tau$

If  $\Psi$  is already an eigenfunction of operator B, then we are certain to observe the value  $b_k$  when  $\Psi = g_k$ .

6. The time development of the state is given by Schrodinger equation:

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

If the *Hamiltonian is independent of time*:  $\Psi(x,t) = e^{-\frac{iE_n t}{\hbar}} \Psi_n(x)$

Then, the experimental observables (probability of finding a particle and expectation value) will not depend on time:

Probability:  $|\Psi(x,t)|^2 = \Psi^*(x,t) \cdot \Psi(x,t) = e^{\frac{iEt}{\hbar}} \cdot \Psi^*(x) \cdot e^{-\frac{iEt}{\hbar}} \cdot \Psi(x) = \Psi^*(x) \cdot \Psi(x)$

Expectation value:  $\langle A \rangle = \int \Psi^*(x,t) \hat{A} \Psi(x,t) dx = \int \Psi^*(x) \hat{A} \Psi(x) dx$  *If operator is independent of time*

Thus, wavefunctions  $\Psi(x,t)$  are called stationary states (note: particle is not stationary)

If the *Hamiltonian is dependent of time*: the new wavefunction can be expressed as an expansion of stationary wavefunctions:

$$\Psi^{ns}(x,t) = \sum_k b_k(t) e^{-\frac{iE_k t}{\hbar}} \Psi^s_k$$

Here, coefficients  $b_k$  depend on time. To obtain these coefficients, we can use time-dependent perturbation theory (chapter 9).

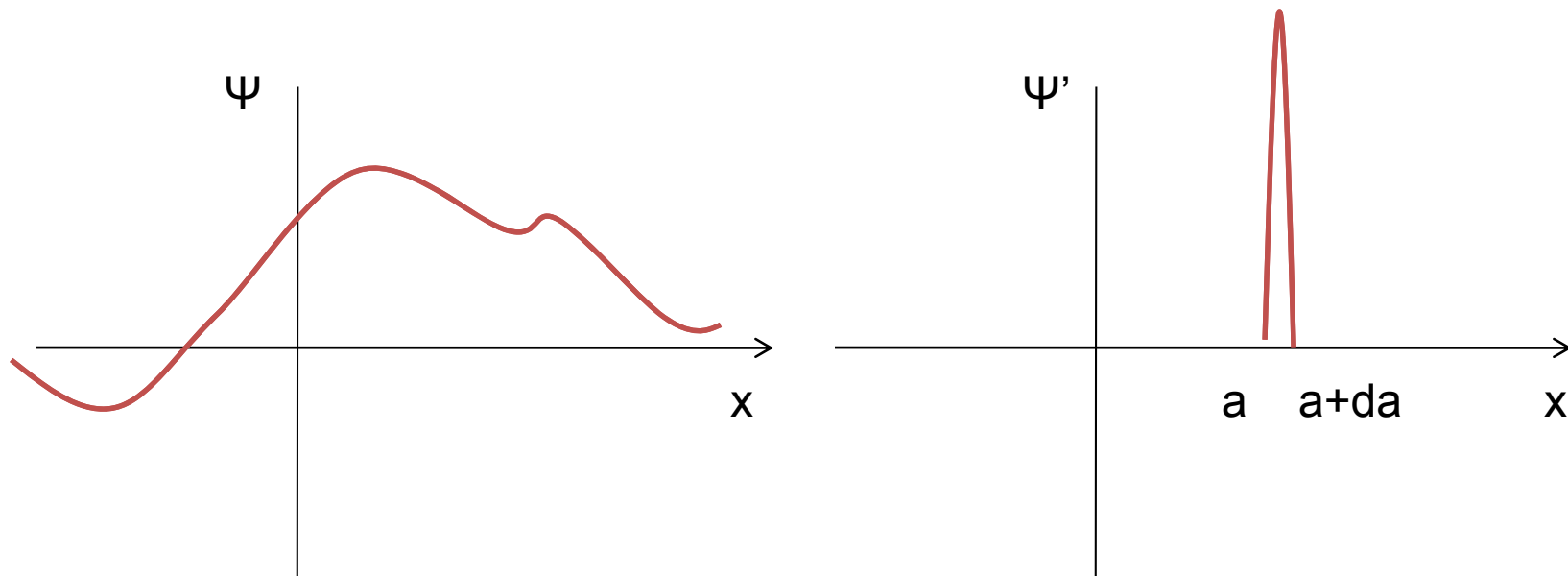
What happens to wavefunction during the measurements?

-The measurement causes a sudden change in the state of a system (collapse of a wavefunction).

*A measurement of the property  $B$  that yields the result  $b_k$  changes the state function to  $g_k$ , the eigenfunction of operator  $B$  whose eigenvalue is  $b_k$ .*

Example: before the measurement of the particle's position, the system is described by a wavefunction  $\Psi$ . The measurement of the position yields that the particle is somewhere around  $x=a$ :  $a < x < a+da$

After the measurement, how does the wavefunction look like? It collapses into  $\Psi'$ :



## Matrices

- Matrix algebra is commonly used in quantum mechanics.
- A matrix is a rectangular array of numbers:

$$A = \begin{pmatrix} a_{11} & a_{12} & \dots & a_{1n} \\ a_{21} & a_{22} & \dots & a_{2n} \\ \cdot & \cdot & \dots & \cdot \\ a_{m1} & a_{m2} & \dots & a_{mn} \end{pmatrix}$$

- Sum of two matrices:  $C=A+B$ :  $c_{ij}=a_{ij}+b_{ij}$
- Product of a matrix with a scalar:  $D=k \cdot A$ :  $d_{ij}=k \cdot a_{ij}$
- Product of two matrices:  $C=A \cdot B$ :  $c_{ij} = \sum_{k=1}^n a_{ik} \cdot b_{kj}$

$m \times p$     $m \times n$     $n \times p$

Example: Calculate  $C=A \cdot B$  for:  $A = \begin{pmatrix} -1 & 3 & \frac{1}{2} \\ 0 & 4 & 1 \end{pmatrix}$   $B = \begin{pmatrix} 1 & 0 & -2 \\ 2 & 5 & 6 \\ -8 & 3 & 10 \end{pmatrix}$

$$c_{11} = a_{11} \cdot b_{11} + a_{12} \cdot b_{21} + a_{13} \cdot b_{31}$$

$$c_{11} = -1 \cdot 1 + 3 \cdot 2 + \frac{1}{2} \cdot (-8) = -1 + 6 - 4 = 1$$

$$C = \begin{pmatrix} 1 & 16\frac{1}{2} & 25 \\ 0 & 23 & 34 \end{pmatrix}$$

- Product is not commutative:  $AB \neq BA$  (in the previous example,  $BA$  is not defined)
- Product is associative:  $A(BC) = (AB)C$
- Product is distributive:  $A(B+C) = AB+AC$
  
- Square matrix: a matrix with equal number of columns and rows.
- Diagonal matrix: a square matrix having zero for all elements except the diagonal ones.
- The trace of a square matrix is the sum of the elements on the principal diagonal. If the size of matrix  $A$  is  $n \times n$ , then:

$$TrA = \sum_{i=1}^n a_{ii}$$

- Unit (identity) matrix: a square matrix with zeros for all elements, except diagonal, which have the value of 1:

$$I = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

The product of matrix with identity matrix gives the same matrix back:  $IB=BI=B$

Matrices in quantum mechanics: *Matrices are used in quantum mechanics to represent operators in given basis sets.* Each element of the matrix is represented as:

$$a_{ij} = \int f_i^* \hat{A} f_j d\tau$$

-Since basis set functions are orthogonal, non-diagonal elements will be zero, and diagonal elements will be the eigenvalues of the given operator.

- The matrix representations of operators in a given basis obey the same rules relations as the operators and functions:

1. Addition of two operators:  $\hat{C} = \hat{A} + \hat{B}$

$$\text{Matrix representation: } C_{ij} = \int f_i^* \hat{C} f_j d\tau = \int f_i^* (\hat{A} + \hat{B}) f_j d\tau = \int f_i^* \hat{A} f_j d\tau + \int f_i^* \hat{B} f_j d\tau = A_{ij} + B_{ij}$$

2. Multiplication of an operator with a constant:  $\hat{D} = k \hat{C}$

$$\text{Matrix representation: } D_{ij} = k \int f_i^* \hat{C} f_j d\tau = k C_{ij}$$

3. Product of two operators:  $\hat{R} = \hat{S} \hat{T}$

$$\text{Matrix representation: } R_{ij} = \int f_i^* \hat{S} \sum_k T_{kj} f_j d\tau = \sum_k \int f_i^* \hat{S} f_j d\tau T_{kj} = \sum_k S_{kj} T_{kj}$$