Principles and Theorems of Quantum Mechanics

The Mathematical formalism of quantum mechanics will be further discussed in this class. This leads to a system of postulates which will be the basis of our subsequent applications. We shall also see that quantum mechanics is not just a collection of postulates and mathematical tricks, but also a physical theory of great mathematical beauty.

1. Orthonormal Functions, Complete sets

If ψ_1 and ψ_2 are wavefunctions of a particle moving in three dimensions corresponding to the different energy levels E_1 and E_2 respectively, then

$$\int \psi_1^* \psi_2 \, d\tau = 0 \qquad (1)$$

The integration being throughout all space, and the functions are said to be orthogonal.

Q: How to derive this? [Hint: Use Green's theorem to convert a volume integral to a surface integral according to $\int_{vol} (\psi \nabla^2 \phi - \phi \nabla^2 \psi) \, d\tau = \int_S (\psi \nabla \phi - \phi \nabla \psi) \vec{n} \, dS$]

$$\psi_2 \nabla^2 \psi_1^* = \psi_2 \frac{-2\mathrm{m}(E_1 - V(x))}{\hbar^2} \psi_1^* \qquad (2)$$

$$\psi_1 \nabla^2 \psi_2^* = \psi_1 \frac{-2\mathrm{m}(E_2 - V(x))}{\hbar^2} \psi_2^* \qquad (3)$$

$$\frac{2\mathrm{m}}{\hbar^2}(E_1 - E_2) \int \psi_1^* \psi_2 \, d\tau = 0 \qquad (4)$$

If ψ_m and ψ_n have

$$\int_a^b \psi_m^* \psi_n \, d\tau = \delta_{mn} \qquad (5)$$

δ_{nm} having the value unity if $m = n$ and zero if $m \neq n$ (Kronecker notation), ψ_m ψ_n are **orthonormal.**

Q: If ψ_1 and ψ_2 are degenerate wavefunctions of the energy level E , can we create a wavefunction, say, ψ_3 that is orthogonal to ψ_1 ? and how?

Complete set

A set of functions $\psi_1, \psi_2, \psi_3, \ldots$ is said to be complete if there is no function, not identically zero,

ϕ which is orthonormal to all the functions ψ_n - in other words, no function exists so that

$$\int_a^b \psi_m^* \phi \, d\tau = 0 \quad \text{, for all } m \tag{6}$$

except $\phi \equiv 0$.

In this case, it is possible to expand an arbitrary function ϕ in the integral (a, b) , as an infinite series of the form

$$\phi = a_1 \psi_1 + a_2 \psi_2 + a_3 \psi_3 + \ldots = \sum_n a_n \psi_n \tag{7}$$

$\phi, \psi_1, \psi_2, \ldots, \psi_n$ are linearly independent. (more on *linear independence* here).

The constant coefficients a_n , which can be complex numbers, can be easily determined

$$a_m = \frac{\int_a^b \psi_m^* \phi \, d\tau}{\int_a^b \psi_m^* \psi_m \, d\tau} \tag{8}$$

Examples: Use Fourier series to represent $f(x)$.

2. Hermitian Operators

An operator of physical significance is obviously one whose eigenvalues are measurable values – Measurable values, whatever they may be, are real.

A linear operator H is called hermitian if for two functions ψ and ϕ

$$\int \psi^* H \phi \, d\tau = \int (H \psi)^* \phi \, d\tau \tag{9}$$

The property of being hermitian is called **hermiticity.**

THEOREM: The momentum operator $-i\hbar\nabla$ is hermitian.

Proof

$$\frac{\partial(\psi^* \psi)}{\partial x} = \psi^* \frac{\partial \psi}{\partial x} + \psi \frac{\partial \psi^*}{\partial x} \tag{10}$$

Integration of equation (10) yields

$$\int \partial \frac{(\psi^* \psi)}{\partial x} d\tau = \int \psi^* \frac{\partial \psi}{\partial x} d\tau + \int \psi \frac{\partial \psi^*}{\partial x} d\tau \tag{11}$$

The integral on the left side vanishes for large values of $|x|$ if the particle is confined to some finite region

$$\int \partial \frac{(\psi^* \psi)}{\partial x} dx\, dy\, dz = \int |\psi^* \psi|_{x=-\infty}^{x=\infty} dy\, dz = 0 \tag{12}$$

Hence

$$\int \psi^* (-i\hbar \frac{\partial}{\partial x}) \psi \, d\tau = \int \psi (i\hbar \frac{\partial}{\partial x}) \psi^* \, d\tau = \int \psi (-i\hbar \frac{\partial}{\partial x} \psi)^* \, d\tau \tag{13}$$

The Laplace operator is a hermitian.

Proof.

It is postulated that all quantum mechanical operators that represent dynamic variables are hermitian.

THEOREM: The eigenfunctions $\psi_1, \psi_2, \psi_3, \dots$ of a hermitian operator Q, belonging to different eigenvalues $q_1, q_2, q_3, \dots$ are orthogonal over Q's region of hermiticity.

Proof.

Schmidt orthogonalization method (the eigenvalues are degenerate)

Let ψ_i and ψ_k be two normalized linearly independent eigenfunctions of the hermitian operator Q, both belonging to the save eigenvalue q :

$$Q\psi_i = q\psi_i, \; Q\psi_k = q\psi_k \tag{14}$$

We form

$$Q(\alpha\psi_i + \beta\psi_k) = q(\alpha\psi_i + \beta\psi_k) = q\psi_k' \tag{15}$$

Suppose

$$\int \psi_i^* \psi_k \, d\tau = c \tag{16}$$

$$\psi_k' = \frac{\psi_k - c\psi_i}{\sqrt{1-c^2}}$$

3. The expectation value and Ehrenfest's theorem

In classical physics, there can be little doubt about the connection between a theoretic prediction and its experimental verification. Now, in the realm of quantum mechanics:

- In what way can we extract a value for a dynamic variable from our theory?
- How is this value related to the outcome of an experiment designed to measure the value?

Note that, because of the uncertainty principles, we cannot determine the parameters of a system with complete accuracy.

- In classical physics, the expectation value of a function can be defined as

$$\langle f(x,y,z)\rangle = \int\int\int P(x,y,z)\, f(x,y,z)\, dx\, dy\, dz \tag{17}$$

  where $P(x,y,z)$ is usually called the **probability density**, or the **weight function.**

- The expectation value of the coordinate vector of the particle is thus

$$\langle \vec{r}\rangle = \int \psi^*(\vec{r})\psi(\vec{r})\vec{r}\, d\tau \tag{18}$$

- How do we define the expectation value of an operator?

$$\langle p_x\rangle = -\int i\hbar \frac{\partial}{\partial x}(\psi^*\psi)\, d\tau \quad ? \tag{19}$$

  Or

$$\langle p_x\rangle = -\int \psi^* i\hbar \frac{\partial \psi}{\partial x}\, d\tau \quad ? \tag{20}$$

- Paul Ehrenfest's method

$$\langle x(t)\rangle = \int x\psi^*\psi\, d\tau \tag{21}$$

$$\langle p_x\rangle = m\frac{d\langle x\rangle}{dt} \tag{22}$$

$$\begin{aligned} m\frac{d\langle x\rangle}{d}t &= m\frac{d}{dt}\int x\psi^*\psi\, d\tau \\ &= m\int x\left(\psi^*\frac{\partial\psi}{\partial t} + \psi\frac{\partial\psi^*}{\partial t}\right)d\tau \end{aligned} \tag{23}$$

  From the time-dependent Schrödinger equation

$$\frac{\partial\psi}{\partial t} = \frac{i\hbar}{2\text{m}}\nabla^2\psi + i\hbar V\psi \tag{24}$$

$$\frac{\partial\psi^*}{\partial t} = \frac{-i\hbar}{2\text{m}}\nabla^2\psi^* - i\hbar V\psi^* \tag{25}$$

$$\langle p_x \rangle = m \int \psi^* x \frac{i\hbar}{2\mathrm{m}} \nabla^2 \psi \, d\tau - m \int \psi \, x \frac{i\hbar}{2\mathrm{m}} \nabla^2 \psi^* \, d\tau \tag{26}$$

Due to the hermiticity of the Laplace operator, the second integral can be rewritten

$$\int x \psi \frac{i\hbar}{2\mathrm{m}} \nabla^2 \psi^* \, d\tau = \int \psi^* \frac{i\hbar}{2\mathrm{m}} \nabla^2 (x\psi) \, d\tau \tag{27}$$

$$\begin{aligned} \langle p_x \rangle &= \frac{i\hbar}{2} \int \psi^* [x \nabla^2 \psi - \nabla^2 (x\psi)] \, d\tau \\ &= \frac{i\hbar}{2} \int \psi^* (x \nabla^2 \psi - 2 \nabla x \nabla \psi - x \nabla^2 \psi) \, d\tau \\ &= i\hbar \int \psi^* \frac{\partial \psi}{\partial x} \, d\tau \end{aligned} \tag{28}$$

$$\langle p_x \rangle = \int \psi^* (-i\hbar \nabla) \psi \, d\tau \tag{29}$$

- Postulate (Dirac): The expectation value of an operator $\hat{F}(-i\hbar\nabla, \vec{r})$ (dynamic variable) is found by letting

$$\langle F \rangle = \int \psi^* \hat{F} \psi \, d\tau \tag{30}$$

ψ Being the normalized wavefunction, the integration being throughout the configuration space of the system.

The superposition of states

Let Q be a hermitian operator with a complete set of normalized eigenfunctions u_k , $k=1,2,3,\ldots$ belonging to the eigenvalues $q_k, k=1,2,3,\ldots$ Let a quantum mechanical system be in a state descriped by a wavefunction ψ_n , which is not a eigenfunction to Q . The expectation value of Q is then

$$\langle Q_n \rangle = \int \psi_n^* Q \psi_n \, d\tau \tag{31}$$

We expand $\psi_n = \sum_{i=0}^{\infty} a_{ni} u_i$.
Substitution into equation (31) yields

$$\langle Q_n \rangle = \int \sum_{i=0}^{\infty} a_{ni}^* u_i^* \sum_{k=0}^{k=\infty} a_{nk} Q u_k \, d\tau \tag{32}$$

Due to the orthonormality of u_i and u_k ,

$$\langle Q_n \rangle = \sum_{i=1}^{\infty} a_{ni}^* a_{ni} q_i = \sum_{i=1}^{\infty} |a_{ni}^2| q_i \tag{33}$$

4. Commutation Relations

The product of two operators, say $\hat{A}\hat{B}$, represents the successive action of the operators, reading from right to left – first $\hat{B}$ then $\hat{A}$. In general, the action of two operators in the reversed order, say, $\hat{B}\hat{A}$, gives a different result, which can be written $\hat{A}\hat{B}\neq\hat{B}\hat{A}$. We say the operators do not commute.

Daily examples of non-commuting actions:

We shower, and we get dressed $\neq$ We get addressed and we shower

The commutator of two operators is defined by

$$[\hat{A},\hat{B}]\equiv\hat{A}\hat{B}-\hat{B}\hat{A} \tag{34}$$

When $[\hat{A},\hat{B}]=0$, the two operators are said to commute. This means their combined effect will be the same whatever order they are applied (like brushing your teeth and showering).

THEOREM: If the linear operators $\hat{A}$ and $\hat{B}$ have a common complete set of eigenfunctions, then $\hat{A}$ and $\hat{B}$ commute, vice versa.

Proof.

Let f be an arbitrary function. Expanding f in terms of the complete set of eigenfuncitons ϕ_i

$$f=\sum_i c_i\phi_i \tag{35}$$

where $\hat{A}\phi_i=a_i\phi_i$ and $\hat{B}\phi_i=b_i\phi_i$
Operating upon the last equation with $\hat{A}\hat{B}-\hat{B}\hat{A}$, we obtain

$$(\hat{A}\hat{B}-\hat{B}\hat{A})f=\sum_i c_i(\hat{A}\hat{B}-\hat{B}\hat{A})\phi_i=\sum_i c_i[\hat{A}(\hat{B}\phi_i)-\hat{B}(\hat{A}\phi_i)] \tag{36}$$

Hence

$$(\hat{A}\hat{B}-\hat{B}\hat{A})f=\sum_i[c_ib_i\hat{A}\phi-c_ia_i\hat{B}\phi]=0 \tag{37}$$

We now prove the converse.

(a) Nondegenerate case.

Let ψ be an eigenfunction to $\hat{A}$

$$\hat{A}\psi=\alpha\psi \tag{38}$$

We now operate upon this equation on both sides with operator $\hat{B}$

$$\hat{B}\hat{A}\psi=\hat{B}\alpha\psi \tag{39}$$

Since $\hat{A}$ and $\hat{B}$ commute,

$$\hat{A}\hat{B}\psi=\alpha\hat{B}\psi \tag{40}$$

i.e., $\hat{B}\psi$ is an eigenfunction of $\hat{A}$, with the eigenvalue α . Since α was assumed to be nondegenerate, $\hat{B}\psi$ can only be a multiple of ψ hence

$$\hat{B}\psi=\beta\psi \tag{41}$$

(b) Degenerate case.

We assume α to be two-fold degenerate and ψ_1 and ψ_2 to be two orthogonal eigenfunctions of $\hat{A}$ belonging to α . We want to prove that any linear combinations of ψ_1 and ψ_2 are also an eigenfunction of $\hat{B}$.

$$\hat{A}\psi=\alpha(a_1\psi+a_2\psi_2) \tag{42}$$

Operating on the last equation with $\hat{B}$ one the left

$$\hat{B}\hat{A}\psi=\hat{B}\alpha(a_1\psi_1+a_2\psi_2) \tag{43}$$

i.e.,

$$\hat{A}\hat{B}\psi=\alpha\hat{B}(a_1\psi_1+a_2\psi_2) \tag{44}$$

$\hat{B}(a_1\psi_1+a_2\psi)$ must be a linear combination of ψ_1 and ψ_2 (do you know why?)

$$\hat{B}(a_1\psi_1+a_2\psi_2)=c_1\psi_1+c_2\psi_2 \tag{45}$$

We need to find c_1 and c_2 that

$$c_1\psi_1+c_2\psi_2=\beta(a_1\psi_1+a_2\psi_2) \tag{46}$$

To this end, let

$$\hat{B}(a_1\psi_1+a_2\psi_2)=\beta(a_1\psi_1+a_2\psi_2) \tag{47}$$

Multiplying equation (46) with ψ_1^* and ψ_2^* , we have

$$a_1\psi_1^*\hat{B}\psi_1+a_2\psi_1^*\hat{B}\psi_2=\beta a_1\psi_1^*\psi_1+\beta a_2\psi_1^*\psi_2 \tag{48}$$

and

$$a_1\psi_2^*\hat{B}\psi_1+a_2\psi_2^*\hat{B}\psi_2=\beta a_1\psi_2^*\psi_1+\beta a_2\psi_2^*\psi_2 \tag{49}$$

We have two simultaneous equations for a_1 and a_2

$$a_1B_{11}+a_2B_{12}=\beta a_1 \tag{50}$$

$$a_1B_{21}+a_2B_{22}=\beta a_2 \tag{51}$$

i.e.,

$$\begin{pmatrix} B_{11}-\beta & B_{12} \\ B_{21} & B_{22}-\beta \end{pmatrix}\begin{pmatrix} a_1 \\ a_2 \end{pmatrix} \equiv 0 \qquad (52)$$

since a_1 and a_2 are arbitrary, the determinant of the their coefficients must vanish

$$\begin{vmatrix} B_{11}-\beta & B_{12} \\ B_{21} & B_{22}-\beta \end{vmatrix} = 0 \qquad (53)$$

This is a quadratic equation with two roots β_1 and β_2 . Therefore c_1 and c_2 can be found according to equation (46), that is, any linear combination of ψ_1 and ψ_2 is also an eigenfunction of $\hat{B}$.

Q: What is the commutator between $[p_x, x]$?

THEOREM: The expectation of two commuting operators can be measured simultaneously with arbitrary precision.

Commutators and the uncertainty principles: If the operators describing two properties of a quantum-mechanical system do not commute, the product of the uncertainties in the measurement of both quantities is larger than or equal to a certain minimum value. This the most general form of the uncertainty principle.

Heisenberg's uncertainty rule: $\Delta x \cdot \Delta p_x > \hbar$

Generally, the uncertainty in a variable is taken to be the root-mean-square deviation from the mean

$$(\Delta x)^2 = \langle (x - \langle x \rangle)^2 \rangle = \langle x^2 \rangle - \langle x \rangle^2 \qquad (54)$$

Similarly,

$$(\Delta p_x)^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 \qquad (55)$$

Constant of motion: Any operator which represents a constant of motion commutes with H .

5. Parity of wavefunctions (symmetry and anti-symmetry)

In general, if ψ is the wavefunction for a nondegenerate state, it must be *symmetric* or *antisymmetric* under any transformation that leaves H unchanged.

Define the reflection operation:

$$R f(x) = f(L-x) \tag{56}$$

$$R\nabla^2 = \frac{\partial^2}{\partial(L-x)^2} = \frac{\partial^2}{\partial x^2} \tag{57}$$

$$RH = H \tag{58}$$

Applying this operator to Schrödinger's equation ($H\psi = E\psi$):

$$(RH)(R\psi) = (RE)(R\psi) \tag{59}$$

For a constant energy E , ψ and $R\psi$ both are eigenstates, which means $R\psi$ is linearly dependent on ψ , that is:

$$R\psi = c\psi \tag{60}$$

with the condition:

$$\int_0^\infty |c\psi^2| d\tau = 1 \tag{61}$$

$$R\psi = \pm\psi \tag{62}$$

$$\psi(x) = \pm\psi(L-x) \tag{63}$$

Parity of wavefunctions:

symmetric ⇔ even parity (*gerade* σ_g)
antisymmetric ⇔ odd parity (*ungerade* σ_u)

6. Postulates of Quantum mechanics

Postulate 1. The state of a system is described by a function of ψ of the coordinates and the time. The square modulus of this function $\psi^* \psi$ gives the probability density for finding the system with a specified set of coordinate values.

Postulate 2. Every observable in quantum mechanics is represented by a linear, hermitian operator.

Postulate 3. In any measurement of an observable A , associated with an operator $\hat{A}$, the only possible results are the eigenvalues a_n , which satisfy an eigenvalue equation $\hat{A}\psi_n = a_n\psi_n$

Postulate 4. For a system in a state described by a normalized wavefunction ψ , the average or expectation value of the observable corresponding to A is given by $\langle A \rangle = \int \psi^* \hat{A} \psi \, d\tau$

Postulate 5. The wavefunction of a system evolves with time in accordance with the time-dependent Schrödinger equation $i\hbar \frac{\partial \Psi}{\partial t} = \hat{H} \Psi$

PROBLEMS: (due Feb. 19, 2008)

1. The wavefunction of a particle is $u(x) = A \exp\left[i\left(\alpha x - \frac{\alpha^2 \hbar t}{2m} \right) \right]$. What is the expectation value of its momentum?

2. Show that the operators L_x , L_y , L_z , representing the componets of the angular momentum of a particle about the origin, satisfy the commutation relations $[L_x, L_y] = i\hbar L_z$, $[L_y, L_z] = i\hbar L_x$, $[L_z, L_x] = i\hbar L_y$.

3. Given the two normalized nonorthogonal functions $(1/\sqrt{\pi})\exp(-r)$ and $\sqrt{1/3\pi}\exp(-r)$, construct a new function ϕ that is orthogonal to the first function and lies with the function space spanned by these two functions, and is normalized.

4. Can we measure the energy and the momentum of a particle simultaneously with arbitrary precision? Why?