

# PRINCIPLES OF QUANTUM MECHANICS

JOE BENTLEY

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## 1. MIXED STATES

If  $\psi_n(x)$  is a solution of the time independent Schrödinger equation, then  $\psi_n(x)$  is an eigenfunction of the Hamiltonian operator with an energy eigenvalue. The full time-dependant form of the wavefunction is given by,

$$\Psi_n(x, t) = \psi_n(x) e^{-\frac{iE_n t}{\hbar}}$$

When we find the probability density, multiply the wavefunction by its complex conjugate. Since the exponential is negative when we take the complex conjugate, they cancel to give,

$$|\Psi_n|^2 = \psi_n^* \psi_n$$

Therefore since  $\psi_n$  has no time dependence, neither does the probability density  $|\Psi_n|^2$ .

Now we consider a mixed state of wavefunctions,

$$\Phi(x, t) = \Psi_m(x, t) + \Psi_n(x, t)$$

By taking the probability density of this,

$$\begin{aligned} |\Phi|^2 &= (\Psi_m + \Psi_n)^* (\Psi_m + \Psi_n) \\ &= \Psi_m^* \Psi_m + \Psi_n^* \Psi_n + \Psi_m^* \Psi_n + \Psi_n^* \Psi_m \end{aligned}$$

The two cross terms at the end of the second line we call the interference terms, which we define as  $z$  and  $z^*$  such that,

$$\begin{aligned} z &= \Psi_m^* \Psi_n = \psi_m^* \psi_n e^{-i(E_n - E_m)t/\hbar} \\ z^* &= \Psi_n^* \Psi_m = \psi_n^* \psi_m e^{i(E_n - E_m)t/\hbar} \end{aligned}$$

We see that this satisfies  $z + z^* = 2\text{Re}\{z\}$ . We can therefore write the probability density as,

$$|\Phi|^2 = |\psi_m|^2 + |\psi_n|^2 + 2\psi_m^* \psi_n \cos\left(\frac{\Delta E t}{\hbar}\right)$$

where  $\Delta E = E_n - E_m$ . Also the assumption has been made that  $\psi_m^* \psi_n$  is a real quantity. We therefore see that the probability density of a mixed state  $\Phi(x, t)$  varies with time unlike previous examples where the probability density function is constant in time. The mixed state  $\Phi$  is an example of a superposition of states. Since Schrödinger's equation is linear, any linear combination of mixed states is also a solution,

$$\Phi = C_m \Psi_m + C_n \Psi_n$$

Note that the time dependent solutions are used here. A mixed state of two time independent solutions,  $\phi(x) = \psi_m(x) + \psi_n(x)$  would not be a solution of the time independent Schrödinger equation, as the energy would need to be well defined, which is isn't for a mixed state,

$$\hat{H}\phi = \hat{H}\psi_m + \hat{H}\psi_n = E_m\psi_m + E_n\psi_n$$

We see that there are two different energies defined, one for each state so this can't be a solution of the time independent Schrödinger equation which has a single well defined energy.

## 2. SUPERPOSITION AND MEASUREMENT

Let  $\Psi_i(x, t)$  where  $i = 1, \dots, n$  form a complete set of solutions to the Schrödinger equation for a given problem. The general solution is then given by,

$$\Phi(x, t) = \sum_{i=1}^n c_i \Psi_i(x, t)$$

where  $c_i$  are complex coefficients. We postulate that *any* valid set of solutions (and thus any valid wavefunction) can be written in this form.

If  $\hat{A}\Psi_i = a_i\Psi_i$  then the observable  $A$  (which corresponds to the operator  $\hat{A}$  and the eigenvalue  $a_i$ ) is well defined for the state. That is,  $\Psi_i$  is an eigenstate of the operator  $\hat{A}$ . The real eigenvalues  $a_i$  represent all the possible results of measuring the observable  $A$  for any state, which must be real as they correspond to an observable  $A$ .

The class of operators that always have real eigenvalues are known as Hermitian operators. An operator  $\hat{o}$  is Hermitian *only* if,

$$\int_{-\infty}^{\infty} \Psi_b^* \hat{o} \Psi_a dx = \int_{-\infty}^{\infty} \Psi_a (\hat{o} \Psi_b)^* dx$$

where  $\Psi_a$  and  $\Psi_b$  are any arbitrary function of  $(x, t)$ . An operator that this is true for is called a self-adjoint operator,

$$\hat{o} = \hat{o}^\dagger$$

A Hermitian matrix is similarly defined,

$$Q = Q^\dagger$$

$$Q_{nm} = Q_{mn}^*$$

We can show that because Hermitian operators are self-adjoint, that they are required to be real. Consider an arbitrary operator  $\hat{o}$  acting on a wavefunction  $\Psi_a$  which is an eigenfunction of the operator  $\hat{o}$ .

$$\text{Let } \hat{o}\Psi_a = a\Psi_a$$

If the operator  $\hat{o}$  is Hermitian, then,

$$\begin{aligned} \int \Psi_a^* \hat{o}\Psi_a dx &= \int \Psi_a (\hat{o}\Psi_a)^* dx \\ \int \Psi_a^* a\Psi_a dx &= \int \Psi_a (a\Psi_a)^* dx \\ a \int \Psi_a^* \Psi_a dx &= a^* \int \Psi_a \Psi_a^* dx \end{aligned}$$

Assuming the wavefunction  $\Psi_a$  is normalized (but even if it isn't, the normalisation constants will cancel anyway),

$$\int \Psi_a^* \Psi_a dx = 1$$

Therefore we come to the conclusion that the Hermitian operator always gives real eigenvalues,

$$a = a^*$$

We postulate that all operators corresponding to observables are Hermitian.

What about the relationship between two different eigenfunctions when the Hermitian is applied? First define  $\Psi_b$  as another eigenfunction of  $\hat{o}$ , such that,

$$\hat{o}\Psi_b = b\Psi_b$$

The Hermitian operator satisfies,

$$\int \Psi_b^* \hat{o}\Psi_a dx = \int \Psi_a (\hat{o}\Psi_b)^* dx$$

Therefore by applying the operator,

$$\begin{aligned} a \int \Psi_b^* \Psi_a dx &= b \int \Psi_a \Psi_b^* dx \\ (a - b) \int \Psi_b^* \Psi_a dx &= 0 \end{aligned}$$

For this to be true we can have two cases. Either  $a = b$  and the integral is one, which implies that  $\Psi_a = \Psi_b$  or just  $\Psi_a = \Psi_a$ , or  $a \neq b$ , which requires that the integral is zero. In this case we say that the eigenfunctions  $\Psi_a$

and  $\Psi_b$  are orthogonal, which we can define succinctly using the Kronecker delta,

$$\int \Psi_b^* \Psi_a dx = \delta_{ab}$$

### 3. EXPECTATION VALUES FOR SUPERPOSITION STATES

Consider the superposition state,

$$\Phi = \sum_{i=1}^n c_i \Psi_i$$

which is a general solution to the Schrödinger equation. We define the operator  $\hat{o}$ , such that  $\Psi_i$  is an eigenfunction, that is,  $\hat{o}\Psi_i = a_i\Psi_i$  where  $a_i$  is a real eigenvalue corresponding to an observable  $o$ . The expectation value of  $o$  can be written as,

$$\langle o \rangle = \int_{-\infty}^{\infty} \Phi^* \hat{o} \Phi dx$$

Assuming that  $\Phi$  is normalized.

We want to show the result of finding the expectation value of a mixed state  $\Phi$ ,

$$\begin{aligned} \langle o \rangle &= \int_{-\infty}^{\infty} \left( \sum_i c_i \Psi_i \right)^* \hat{o} \left( \sum_j c_j \Psi_j \right) dx \\ &= \int_{-\infty}^{\infty} \sum_i c_i^* \Psi_i^* \sum_j c_j a_j \Psi_j \\ &= \sum_i \sum_j c_i^* c_j a_j \int_{-\infty}^{\infty} \Psi_i^* \Psi_j dx \\ &= \sum_i \sum_j c_i^* c_j a_j \delta_{ij} \end{aligned}$$

We know that the integral can be written as the Kronecker delta, because it is normalized, it obeys,

$$\delta_{ij} = \begin{cases} 0 & i \neq j \\ 1 & i = j \end{cases}$$

This is because, as we showed before, if  $i \neq j$  the wavefunctions  $\Psi_i$  and  $\Psi_j$  are orthogonal, and thus the integral over them is zero. If  $i = j$ , due to normalization, the integral over them is one. Therefore the Kronecker delta is satisfied.

Since the Kronecker delta is zero for indices where  $i \neq j$  we can rewrite the expectation value as a single sum,

$$\begin{aligned}\langle o \rangle &= \sum_j c_j^* c_j a_j \\ \langle o \rangle &= \sum_j |c_j|^2 a_j\end{aligned}$$

Remember that  $c_i$  is the weighting of the wavefunction  $\Psi_i$  in the mixed state. The expectation is the weighted mean of all possible values of the eigenvalue and therefore, we can say that  $|c_j|^2$  is the probability of measuring  $a_j$  in any one measurement.

Furthermore, since  $|c_j|^2$  is the probability, it is implied that  $\sum_j |c_j|^2 = 1$ , which we can show,

$$\begin{aligned}\int_{-\infty}^{\infty} \Phi^* \Phi dx &= 1 \\ \int_{-\infty}^{\infty} \sum_i c_i^* \Psi_i^* \sum_j c_j \Psi_j dx &= 1 \\ \sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} \Psi_i^* \Psi_j dx &= 1 \\ \sum_i \sum_j c_i^* c_j \delta_{ij} &= 1 \\ \sum_j |c_j|^2 &= 1\end{aligned}$$

Therefore we have shown,

$$\int_{-\infty}^{\infty} \Phi^* \Phi dx = \sum_j |c_j|^2 = 1$$

#### 4. EXAMPLE: EXPECTATION VALUE

Consider a particle confined in a potential well of width  $a$  with a spatial wavefunction given by,

$$\phi(x) = \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right)$$

The wavefunction  $\phi(x)$  is an eigenstate of the kinetic energy  $T$ ,

$$\hat{T} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} \rightarrow E = \frac{\pi^2 \hbar^2}{2ma^2}$$

However it is not an eigenstate of the momentum operator,

$$\hat{p} = -i\hbar \frac{d}{dx}$$

Eigenfunctions of  $\hat{p}$  can be written in the form,

$$\begin{aligned}\psi_+(x) &= \frac{1}{\sqrt{a}} e^{\frac{i\pi x}{a}} \\ \psi_-(x) &= \frac{1}{\sqrt{a}} e^{-\frac{i\pi x}{a}}\end{aligned}$$

Note that they are normalized with the normalization constants that can be calculated,

$$A^2 \int_{-a}^a \psi_+^* \psi_+ dx = 1 \rightarrow A = \frac{1}{\sqrt{a}}$$

We can write our superposition  $\phi(x)$  in terms of these two eigenfunctions of  $\hat{p}$  by rewriting  $\cos$  in its exponential form,

$$\phi(x) = \sqrt{\frac{2}{a}} \left( \frac{e^{\frac{i\pi x}{a}} + e^{-\frac{i\pi x}{a}}}{2} \right)$$

By some rearrangement we can write this in terms of our eigenfunctions of  $\hat{p}$ ,

$$\phi(x) = \frac{1}{\sqrt{2}} \psi_+(x) + \frac{1}{\sqrt{2}} \psi_-(x)$$

Writing this in the form  $\phi = \sum_i c_i \psi_i$ ,

$$\phi(x) = c_+ \psi_+(x) + c_- \psi_-(x)$$

The probability of measuring each eigenvalue of momentum is thus given by,

$$\begin{aligned}p_+ &= \frac{\hbar\pi}{a} \rightarrow P = |c_+|^2 = \frac{1}{2} \\ p_- &= -\frac{\hbar\pi}{a} \rightarrow P = |c_-|^2 = \frac{1}{2}\end{aligned}$$

We can see that in  $\phi$  is contained two superimposed eigenfunctions that are eigenfunctions of  $\hat{p}$ , while  $\phi$  itself isn't an eigenstate of  $\hat{p}$ .

The expectation value of  $p$  is given by,

$$\langle p \rangle = \frac{1}{2} \left( \frac{\hbar\pi}{a} \right) - \frac{1}{2} \left( \frac{\hbar\pi}{a} \right) = 0$$

In general for a superposition state of many wavefunctions given by  $\phi(x) = \sum_i c_i \psi_i(x)$  we need to use the orthogonality of the wavefunctions to extract the coefficients  $c_j$ ,

$$\begin{aligned} \int \psi_j^* \phi dx &= \sum_i c_i \int \psi_j^* \psi_i dx \\ &= \sum_i c_i \delta_{ij} \\ &= c_j \end{aligned}$$

We call the integral on the left an overlap integral as we are finding how the eigenfunction  $\psi_j^*$  overlaps with the superposition of eigenstates  $\phi$ .

Using this overlap integral we can calculate the weightings  $c_j$  from the previous example, checking that they give us the same answer as before,

$$\begin{aligned} c_+ &= \int_{-a/2}^{a/2} \psi_+^*(x) \phi(x) dx \\ &= \int_{-a/2}^{a/2} \left( \frac{1}{\sqrt{a}} \right)^* \left( \sqrt{\frac{2}{a}} \cos\left(\frac{\pi x}{a}\right) \right) dx \\ &= \frac{\sqrt{2}}{a} \int_{-a/2}^{a/2} \left( \cos\left(\frac{\pi x}{a}\right) - i \sin\left(\frac{\pi x}{a}\right) \right) \cos\left(\frac{\pi x}{a}\right) dx \\ &= \frac{\sqrt{2}}{a} \int_{-a/2}^{a/2} \cos^2\left(\frac{\pi x}{a}\right) dx \\ &= \frac{1}{a\sqrt{2}} \int_{-a/2}^{a/2} \left( 1 + \cos\left(\frac{2\pi x}{a}\right) \right) dx \\ &= \frac{1}{\sqrt{2}} \end{aligned}$$

In the third line we noticed that  $\sin(x)\cos(x)$  is zero over symmetric limits, so we know that term will be zero. We also noticed in the second to last line,  $\cos(x)$  is zero over symmetric limits, so that also goes.

The weighting is thus given by  $c_+ = \frac{1}{\sqrt{2}}$  and is the same as we found before. This is a general method that can be used to find  $c_j$  for any eigenfunction in a superposition of eigenstates, as long as  $\phi(x)$  and  $\psi_j(x)$  are known.

## 5. SUMMARY

Consider a particle in a superposition of eigenstates (that are solutions to the Schrödinger equation) as described by,



$$\Phi(x, t) = \sum_i c_i \Psi_i(x, t)$$

The individual states are eigenfunctions of the hamiltonian, such that,

$$\hat{H}\Psi_i = i\hbar \frac{\partial}{\partial t} \Psi_i$$

where  $\hat{H} = \frac{\hat{p}^2}{2m} + V(x, t)$ .

In cases where the potential  $V$  is only dependent on space, and not time, we can write the superposition in the form,

$$\begin{aligned} \Phi(x, t) &= \sum_j c_j \psi_j(x) e^{-\frac{iE_j t}{\hbar}} \\ \phi(x) &= \sum_i c_i \psi_i(x) \end{aligned}$$

Let  $\psi_i(x)$  where  $i = 1 \dots n$  be eigenfunctions of the operator  $\hat{o}$  such that  $\hat{o}\psi_i = a_i\psi_i$ . What happens when the observable  $o$  is measured? The result will be one of the possible eigenvalues  $a_j$ , with a probability of measuring the particle in that eigenvalue given by  $|c_j|^2$ . If we measure the observable  $o$  again on the same particle, the result will be the same eigenvalue  $a_j$ , but it will be *certain*. That is, repeated measurements of  $o$  will give the same eigenvalue  $a_j$  with a probability of unity. This is because the measurement of a eigenvalue is said to collapse the wavefunction from being a superposition of multiple eigenstates to one specific eigenstate. That is, instead of the particle being in a superposition of eigenstates  $\phi(x)$  is collapses to one eigenstate  $\psi(x)$ . The act of measuring the quantity itself causes this collapse.

Measurement of the same observable  $o$  on *many* particles will yield different results each time, with the average result given by the expectation value,

$$\langle o \rangle = \sum_i |c_i|^2 a_i$$

## 6. SIMULTANEOUS EIGENFUNCTIONS

A wavefunction can be an eigenfunction of more than one operator at the same time. For example consider the free particle wavefunction,

$$\Psi(x, t) = Ae^{i(kx - \omega t)}$$

This is an eigenfunction of both the energy operator  $\hat{E}$  and the momentum operator  $\hat{p}$ ,

$$\begin{aligned}\hat{p} &= -i\hbar \frac{\partial}{\partial x} & \hat{p}\Psi &= p\Psi & p &= \hbar k \\ \hat{E} &= i\hbar \frac{\partial}{\partial t} & \hat{E}\Psi &= E\Psi & E &= \hbar\omega\end{aligned}$$

However it is not generally true that wavefunctions are eigenstates of both  $\hat{p}$  and  $\hat{E}$ . This happens when the operators commute. Commutation is when the order of operations don't matter, for example numbers are commutative under multiplication and addition, that is  $xy = yx$  and  $y + x = x + y$ . Operators however do not usually commute,

$$x \frac{d}{dx} (f(x)) \neq \frac{d}{dx} (xf(x))$$

In quantum mechanics, operators generally don't commute either,

$$\begin{aligned}\hat{A}(\hat{B}\psi) &\neq \hat{B}(\hat{A}\psi) \\ (\hat{A}\hat{B} - \hat{B}\hat{A})\psi &\neq 0\end{aligned}$$

We call the left hand side of the second line the commutator of  $\hat{A}$  and  $\hat{B}$ , and write it as  $[\hat{A}, \hat{B}]$ . If  $[\hat{A}, \hat{B}] = 0$  the operators are said to commute. Note that this condition is independent of  $\psi$ , as if  $\psi$  is zero then it does not describe the particle at all. This means that we can write,

$$\begin{aligned}\text{if } [\hat{A}, \hat{B}] &\neq 0 & \hat{A} \text{ and } \hat{B} &\text{ do not commute} \\ \text{if } [\hat{A}, \hat{B}] &= 0 & \hat{A} \text{ and } \hat{B} &\text{ commute}\end{aligned}$$