PRINCIPLES OF QUANTUM MECHANICS

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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 ψ_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,

$$|\Phi|^2 = (\Psi_m + \Psi_n)^*(\Psi_m + \Psi_n)$$
$$= \Psi_m^* \Psi_m + \Psi_n^* \Psi_n + \Psi_m^* \Psi_n + \Psi_n^* \Psi_m$$

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,

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

We see that this satisfies $z + z^* = 2Re\{z\}$. 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 Φ 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 $i = 1, \ldots, n$ 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, Ψ_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 Ψ_a and Ψ_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 Ψ_a which is an eigenfunction of the operator $\hat{o}$.

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

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

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

$$\int \Psi_a^* a\Psi_a dx = \int \Psi_a (a\Psi_a)^* dx$$

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

Assuming the wavefunction Ψ_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 Ψ_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,

$$a \int \Psi_b^* \Psi_a dx = b \int \Psi_a \Psi_b^* dx$$

$$(a - b) \int \Psi_b^* \Psi_a dx = 0$$

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 Ψ_a

and Ψ_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 Ψ_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 Φ is normalized.

We want to show the result of finding the expectation value of a mixed state Φ,

$$\langle o \rangle = \int_{-\infty}^{\infty} \left(\sum_i c_i \Psi_i \right)^* \hat{o} \left(\sum_j c_j \Psi_j \right) dx$$

$$= \int_{-\infty}^{\infty} \sum_i c_i^* \Psi_i^* \sum_j c_j a_j \Psi_j$$

$$= \sum_i \sum_j c_i^* c_j a_j \int_{-\infty}^{\infty} \Psi_i^* \Psi_j dx$$

$$= \sum_i \sum_j c_i^* c_j a_j \delta_{ij}$$

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 Ψ_i and Ψ_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,

$$\langle o \rangle = \sum_j c_j^* c_j a_j$$

$$\langle o \rangle = \sum_j |c_j|^2 a_j$$

Remember that c_i is the weighting of the wavefunction Ψ_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,

$$\int_{-\infty}^{\infty} \Phi^* \Phi \, dx = 1$$

$$\int_{-\infty}^{\infty} \sum_i c_i^* \Psi_i^* \sum_j c_j \Psi_j \, dx = 1$$

$$\sum_i \sum_j c_i^* c_j \int_{-\infty}^{\infty} \Psi_i^* \Psi_j \, dx = 1$$

$$\sum_i \sum_j c_i^* c_j \delta_{ij} = 1$$

$$\sum_j |c_j|^2 = 1$$

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,

$$\psi_+(x) = \frac{1}{\sqrt{a}} e^{\frac{i\pi x}{a}}$$

$$\psi_-(x) = \frac{1}{\sqrt{a}} e^{-\frac{i\pi x}{a}}$$

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,

$$p_+ = \frac{\hbar \pi}{a} \rightarrow P = |c_+|^2 = \frac{1}{2}$$

$$p_- = -\frac{\hbar \pi}{a} \rightarrow P = |c_-|^2 = \frac{1}{2}$$

We can see that in ϕ is contained two superimposed eigenfunctions that are eigenfunctions of $\hat{p}$, while ϕ 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 $\phi(x) = \sum_i c_i \psi_i(c)$ we need to use the orthogonality of the wavefunctions to extract the coefficients c_j,

$$\int \psi_j^* \phi \, dx = \sum_i c_i \int \psi_j^* \psi_i \, dx$$
$$= \sum_i c_i \delta_{ij}$$
$$= c_j$$

We call the integral on the left an overlap integral as we are finding how the eigenfunction ψ_j^* overlaps with the superposition of eigenstates ϕ.

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,

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

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,

$$\Phi(x,t) = \sum_j c_j \psi_j(x) e^{-\frac{iE_j t}{\hbar}}$$

$$\phi(x) = \sum_i c_i \psi_i(x)$$

Let $\psi_i(x)$ where $i = 1\ldots n$ 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,

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

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

$$\hat{p} = -i\hbar\frac{\partial}{\partial x} \qquad \hat{p}\Psi = p\Psi \qquad p = \hbar k$$

$$\hat{E} = i\hbar\frac{\partial}{\partial t} \qquad \hat{E}\Psi = E\Psi \qquad E = \hbar\omega$$

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 $y + x = y + x$. Operators however do not usually commute,

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

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

$$\hat{A}(\hat{B}\psi) \neq \hat{B}(\hat{A})$$

$$(\hat{A}\hat{B} - \hat{B}\hat{A})\psi \neq 0$$

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 ψ, as if ψ is zero then it does not describe the particle at all. This means that we can write,

$$\text{if } [\hat{A}, \hat{B}] \neq 0 \quad \hat{A} \text{ and } \hat{B} \text{ do not commute}$$

$$\text{if } [\hat{A}, \hat{B}] = 0 \quad \hat{A} \text{ and } \hat{B} \text{ commute}$$

We can show that $\hat{A}$ and $\hat{B}$ commute if they share a complete set of eigenfunctions quite easily.

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

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

Here we have two operators for which ψ_i are eigenfunctions of for any i, where ψ_i for all i represent a complete set of solutions to the Schrödinger equation. Therefore by applying the commutator to the eigenfunction,

$$\begin{aligned}
\left[\hat{A}, \hat{B}\right]\psi_i &= \hat{A}\hat{B}\psi_i - \hat{B}\hat{A}\psi_i \\
&= \hat{A}(b_i\psi_i) - \hat{B}(a_i\psi_i) \\
&= a_ib_i\psi_i - b_ia_i\psi_i \\
&= 0
\end{aligned}$$

Therefore we have shown that two operators $\hat{A}$ and $\hat{B}$ commute, for any eigenfunction of $\hat{A}$ and $\hat{B}$.

This also holds true for any superposition of eigenstates, as a superposition state is just a linear combination of eigenstates,

$$\phi = \sum_{i=1}^{n} c_i \psi_i$$

and then by applying the commutator,

$$\left[\hat{A}, \hat{B}\right] \psi_i = \sum_{i=1}^{n} c_i \left[\hat{A}, \hat{B}\right] \psi_i = 0$$

So now that we have the mathematics that we need in applying the commutator, how can we relate this to actually measuring an eigenvalue? Let us consider the situation where we measure two observables A and B, in that order, first A, and then B.

First we measure A, the result is the eigenvalue a_j with probability given by $|c_j|^2$. This, as we have seen before, collapses the wavefunction from a superposition of eigenstates to one eigenstate ψ_j.

When we take the next measurement, the measurement of B, we get the result b_j with a probability of unity. This is because we have *already* collapsed the superposition of eigenstates to a single eigenstate ψ_j by the act of measurement. Therefore when we apply the operator $\hat{B}$ we just obtain a single eigenvalue with no uncertainty.

We have therefore shown that if two operators commute, such that $\left[\hat{A}, \hat{B}\right] = 0$, then it is possible to measure both A *and* B simultaneously with no uncertainty. However it is not generally the case, and we will next explore what happens when they do *not* commute.

For example, take the position and momentum operators, $\hat{x}$ and $\hat{p_x}$. We can easily show that they do not commute,

$$\begin{aligned}
[\hat{x}, \hat{p_x}] \psi &= \left[x, -i\hbar \frac{\partial}{\partial x}\right] \psi \\
&= -i\hbar \left(x \frac{\partial \psi}{\partial x} - \frac{\partial}{\partial x}(x\psi) \right) \\
&= -i\hbar \left(x \frac{\partial \psi}{\partial x} - \psi - x \frac{\partial \psi}{\partial x} \right) \\
&= i\hbar \psi
\end{aligned}$$

Therefore we have shown that for *any* wavefunction ψ, the position and momentum operators do not commute. This implies that $\hat{x}$ and $\hat{p_x}$ do not share a simultaneous set of eigenfunctions. We therefore can not know both

x and p_x simultaneously. This can be related to the Heisenberg Uncertainty Principle.

Let us define uncertainty as the statistical mean-square deviation of a distribution. The standard deviation squared is given by,

$$(\Delta A)^2 = \langle (A - \langle A \rangle)^2 \rangle = \langle A^2 \rangle - \langle A \rangle^2$$

It can be shown that the product of the uncertainty for any two observables can be related to the commutator of the operators relating to those observables. A proof for this will not be shown here however, this relation is given by,

$$(\Delta A)^2 (\Delta B)^2 \geq \frac{1}{4} \left| \left\langle \left[\hat{A}, \hat{B} \right] \right\rangle \right|^2$$

For example, applying this to the position and momentum,

$$(\Delta x)^2 (\Delta p_x)^2 \geq \frac{1}{4} \hbar^2$$

and thus we obtain the Heisenberg Uncertainty Principle,

$$\Delta x \Delta p \geq \frac{\hbar}{2}$$

Uncertainty relations exist for any non-commuting pair of operators. For example we can show the same thing for energy and time, by showing that the commutator is the same as for momentum and position.