

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 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,

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

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 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 $i = 1, \dots, n$ 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, 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} .

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

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 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,

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

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 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 ,

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

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 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,

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

Remember that c_i is the weighting of the wavefunction 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,

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

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 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 $\phi(x) = \sum_i c_i \psi_i(x)$ 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 ψ_j^* overlaps with the superposition of eigenstates ϕ .