

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,

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

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,

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