



STUDY MATERIAL

VIVEKANANDA COLLEGE THAKURPUKUR

NAAC ACCREDITED GRADE—'A'

Subject: Chemistry

**Topic: On Wave Functions: Interpretation
and Acceptability Criteria**

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The time-independent Wave function

The very first postulate of wave mechanics says that a dynamical system is completely represented by a function Ψ , which is a complex function (in general) and it contains all information about the system under consideration. It is called a 'state function', or 'wave function' or 'probability amplitude function'. For example, for a single particle executing motion in one dimensional space, Ψ depends on x and t (time). For a single particle in 3-dimensional space, it will depend on x, y, z and t . For two-particle system Ψ will depend on $x_1, y_1, z_1, x_2, y_2, z_2$ and t , where (x_1, y_1, z_1) and (x_2, y_2, z_2) are the space coordinates of particles 1 and 2 respectively.

However, for 'stable' / 'stationary' / time-independent states of the system we have special solutions. The space and time parts are separable, and the space-dependent part of the solution can describe the system sufficiently. Let us call that part $\psi(x)$, for a single-particle moving in one-dimensional space. It is the solution to the time-independent Schrödinger Equation (eigenvalue equation):

$$\hat{H} \psi(x) = E \psi(x)$$

Once we find the solution $\psi(x)$, we can predict the value of total energy of the particle (E) in the state $\psi(x)$, by operating \hat{H} on $\psi(x)$.

The Physical interpretation of Wave function

The wave function Ψ as such cannot have any physical significance as it is a complex function. Max Born associated a physical significance with it, by multiplying it with its complex conjugate, to remove the complex part.

If the state of a single particle executing motion in one dimensional space is represented by Ψ , then $\Psi^* \Psi dx$ is the probability of finding the particle within the space x to $x+dx$ at a particular instant t .

For a particle moving in three-dimensional space, $\Psi^* \Psi dx dy dz$ is the probability of finding the particle within the space x to $x+dx$, y to $y+dy$, and z to $z+dz$, at a particular instant t .

The name 'probability amplitude function' given to wave functions conforms to this physical significance.

For two particle system $\Psi^* \Psi dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$ will be the probability of finding the particle 1 within the space x_1 to x_1+dx_1 , y_1 to y_1+dy_1 , and z_1 to z_1+dz_1 , and the particle 2 within the space x_2 to x_2+dx_2 , y_2 to y_2+dy_2 , and z_2 to z_2+dz_2 , at a particular instant t , where (x_1, y_1, z_1) and (x_2, y_2, z_2) are the space coordinates of particles 1 and 2 respectively. In general, we can represent elements like $dx_1 dy_1 dz_1 dx_2 dy_2 dz_2$ as simply $d\tau$ (the relevant hypervolume element). $\Psi^* \Psi dx$ is the same as $|\Psi|^2 / dx$.

The Well-behaved Wave function

As soon as we associate the wave function Ψ (the modulus of Ψ , to be precise) with a physical significance, it must satisfy certain criteria, to be acceptable. Some mathematical functions (called well-behaved, for obvious reasons) conform to these criteria, and only those functions are fit to represent the dynamical state of a system. These are:

1. Ψ must be continuous, finite and single-valued.
2. The first derivative of Ψ should also be continuous, finite and single-valued. (If it is discontinuous, then the second derivative of Ψ will be infinite)
3. Ψ should be quadratically integrable, and normalized. That is,

$$\int \psi^* \psi d\tau = \int |\psi|^2 d\tau = 1$$

The integral is over all space relevant to the system (from $+\infty$ to $-\infty$, 0 to ∞ , 0 to any constant value, any limit depending on the system)

For example, for a single particle executing motion in one dimensional space, the limit of summation of $\psi^* \psi dx$ over the whole (relevant) space must be equal to the total probability of finding the particle anywhere in the whole space, which is unity.

This is called the Normalization condition.

Orthogonality of Eigenfunctions

For a system we have a complete set of time-independent wave functions ψ_i which are eigenfunctions of the total energy operator, all of them tagged to their specific eigenvalues E_i . Any non-eigenstate can be represented by a linear combination of these wave functions. These eigenfunctions are orthogonal to each other, which means that any two eigenfunctions, say, ψ_i and ψ_j (where $i \neq j$) satisfy the condition:

$$\int \psi_i^* \psi_j d\tau = 0$$

The integral is over all space relevant to the system.

This is called the Orthogonality condition

There exist complete sets of eigenfunctions of other quantum mechanical operators too (each operator representing a measurable property of the system). For example, we have complete sets of eigenfunctions of momentum coordinates, space coordinates, angular momenta etc. **Operating the relevant operators on them, we can predict eigenvalues, those which will be observed on measurement of that property. All of these sets of eigenfunctions satisfy the 'orthonormality' condition, so that they are physically significant.**