Quantum Mechanics

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Some Basic Concepts

In 1924, Louis de Broglie suggested on theoretical grounds that any particle, not only photons travelling with a momentum p, should have (in some sense) a wavelength given by the de Broglie relation i.e. $\lambda = \frac{h}{p}$

Macroscopic bodies have such a light momenta that their wavelength are undetectably small and their wave properties cannot be observed. The momentum of a single photon on the other hand (specially for long wavelength electromagnetic radiations - UV, visible and longer.) may be calculated using the above relation as having very small values. The particle like properties of such radiations thus were not noticed for a long time.

Be that as it may, today we know that not only do electromagnetic radiations have characteristics of particles, but electrons (and other particles) have the characteristics of waves. This joint particle and wave character of matter and radiation is called as **Wave Particle Duality**.

In chemistry we would like to have a theoretical understanding of the dynamics and distribution of electrons in atoms and molecules. If w consider electrons simply as particles and apply the principles of Classical Newtonian mechanics then it has been shown, we miserably fail to explain the properties of atoms and molecules (eg. atomic spetra).

The new mechanics based on the whole set of basic concepts, has been devised for studying the dynamics of microscopic systems. This new mechanics takes into cognizance the wave particle duality among other things and is what is known as Quantum Mechanics.

We begin by supposing that the position of a particle is distributed through space like the amplitude of a wave. The description does seem mysterious to the uninitiated. The problem lies in our attempting to visualize such a behaviour of a particle in terms of analogies with what we 'seen', 'observed' or 'studied'. So for our purpose the best approach would be to accept the wave description given above as an axiom. Very soon in our discussion we will come up with results which we can relate with more

visualizable concepts.

The wave that in quantum mechanics replaces the classical concept of trajectory (of particle) is called **Wave Function** and denoted ψ.

General features of Wave Function

The following feature of the wavefunction ψ could be kept in our minds to start with. We will add on further features as we develop our ideas for studying the dynamics of electrons in atoms and molecules.

- A wavefunction is just a mathematical function ex. $\psi = sinx$ or $\psi = e^{-ax}$ could be a wavefunction.

- The wavefunction contains all the information that is possible to know about the location and motion of a particle is describes.

- If a wave function is large at a particular point, then the probability of the particle being at that point is high. If the wavefunction is zero at a point, then the particle will never be found there. A point would simply mean a particular value of x.

- The more rapaidly a wavefunction changes from palce to place, the higher the kinetic energy of the particle it describes.

In 1926, Erwin Schrödinger proposed an equation for finding the wavefunction of any system. For a particle of mass **m** moving in one dimension with energy **E** and if **V(x)** which is a function of x (i.e. it depends on the position of the particle) is the potential energy of the particle then,

$$-\frac{\hbar^2}{2m}\frac{\partial^2\psi}{\partial x^2} + V(x)\psi = E\psi \; where \; \hbar = \frac{h}{2\pi} \tag{1}$$

If we consider an operator $H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x) = -\frac{\hbar^2}{2m}\nabla + V(x)$, then we get the general form of the Schrödinger equation which is,

$$H\psi = E\psi$$

In the above simple case $\nabla^2 = \frac{\partial^2}{\partial x^2}$. In the case for the three dimensional motion defined in the Cartesian coordinate system,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

If we solve the Schrödinger equation for a particle such as an electron, moving in a straight line (the equation (1)) in a region of uniform potential (i.e. V(x)=constant) then one solution gives $\psi = e^{\iota kx} = coskx \pm \iota sinkx$. Here ψ represents a wave of wavelength,

$$\lambda = \frac{2\pi}{k} \tag{2}$$

where,

$$k = \left(\frac{2mE_{KE}}{\hbar^2}\right)^{\frac{1}{2}} \tag{3}$$

Here, the Kinetic energy, E_{KE} is defined as,

$$E_{KE} = \frac{p^2}{2m} \tag{4}$$

where **p** is the momentum of the particle. Substituting equation (4) in equation (3) we get,

$$k = \left(\frac{2m * \frac{p^2}{2m}}{\hbar^2}\right)^{\frac{1}{2}} = \frac{p}{\hbar}$$

$$or, p = k\hbar = \frac{kh}{2\pi} \tag{5}$$

But, from equation (2) and substituting this in equation (5) we have $p = \frac{2\pi}{\lambda}\frac{h}{2\pi} = \frac{h}{p}$ which is nothing but the de Broglie equation. Thus, thought the Schrödinger equation is a postulate like Newtons equations of motion, we see that at least for a freely moving particle, it simply implies the de Broglie relation.

What now is the meaning of ψ and its wavelength λ? We answer the latter question first. Using equations (2) and (3) above we can show

$$\lambda = \frac{h}{(2mE_{KE})^{\frac{1}{2}}} \tag{6}$$

Clearly, a large KE means a short wavelength and vice-versa. For a stationary particle, $E_{KE} = 0$ and λ becomes infinite. It means that the wavefunction ψ has the same value everywhere. $\psi =$ constant for a particle at rest, If the kinetic energy is high and hence the wavelength is short then the value of ψ (or its amplitude) will change very quickly from point to point. Compare the conclusion with the last point listed under the 'General features of a wave function' earlier,

For understanding the meaning of ψ in terms of the location of the particle we take recourse to the "Born interpretation" due to Max Born. ψ has different values at different points and maybe related to the amplitude of the wave at a point. For electro-magnetic waves, the intensity in a region is interpreted as the square of the amplitude in that region. And the intensity of a wave is a measure of the probability of finding a photon present in that region.

The Born Interpretation of the wave function is that the value of ψ^2 (or $\psi^*\psi$ if ψ is a complex function) at a point is proportional to the probability of finding the particle at that point.

Thus the wave function ψ is called the **Probability Amplitude** and $\psi^*\psi$ is the **Probability Density**. If we find the value of $\psi^*\psi$ in an infinitesimally small region $d\tau = $ dx.dy.dz then $\psi^*\psi d\tau$ is proportional to the probability if finding the particle in the region $d\tau$ (probability = probability density * volume in the same way as mass=density * volume).

It is important to note that ψ, the probability amplitude may be positive or negative (and in general a complex quantity. This means it takes a form such as $(a + \iota b)$ where $\iota = \sqrt{-1}$). But we need not bother about its physical interpretation since $\psi^*\psi$ or $\mid \psi \mid^2$ or the square modulus of ψ, is real and never negative.

Notice also the difference between a wave function and waves that we are familiar with - such as water waves. In the case of water waves the negative value of the amplitude means low water level and the positive value of the amplitude means high water level. But for a wave function, a large positive value or a large negative value imply large probabilities of finding the particle

It is also important to note that the positive and negative sign of ψ has nothing to do with the electrical charge on a particle. Nor does a negative value of ψ mean that the particle is missing from the region. What then is the significance of ψ!

For one thing, ψ has no physical meaning, - only $\psi^*\psi$ or $\mid \psi \mid^2$ has a definite physical meaning and is of direct significance. On the other hand, the sign of ψ has an indirect significance. We will find out more about it when we will have to super impose more than one wavefunctions. There we will talk about constructive and destructive interference in order to determine the resultant wavefunction.

Restrictions due to Schrödinger equation

The Schrödinger equation has in principle an infinite number of solutions. But for a solution to be physically significant, it should be amenable to the Born interpretation as outlined above. The Born interpretation poses severe restrictions on the possible solutions of the Schrödinger equation and the latter itself puts severe mathematical restrictions on the nature of ψ.

In order that the equation be valid everywhere and the equation involves $\nabla^2\psi$, the value of $\nabla^2\psi$ must be defined everywhere. Mathematically it means that $\nabla\psi$ must be continuous and if $\nabla\psi$ has to be continuous then, ψ must be continuous. **In graphical terms, the plot of ψ must be continuous having no sharp steps and its slope also must be continuous that is there are no kinks**.

In order that $\mid \psi \mid^2$ must represent the probability of finding a particle,

- $\int_{wholespace} \mid \psi \mid^2 d\tau = 1$ i.e. the probability of finding the particle anywhere in space is unity. This is called as **Normalization Condition**. In itself it does not pose much of a problem. If we have otherwise acceptable solution ψ for the equation $H\psi = E\psi$ then we can always say that $N\psi$ is also a solution if N is a constant (normalization constant). We simply have to impose the condition,

$$\int (N\psi^2)(n\psi)d\tau = \int N^2 \mid \psi \mid^2 d\tau = N^2 \int \mid \psi \mid^2 d\tau = 1$$

$$or, N = \sqrt{\frac{1}{\int \mid \psi \mid^2 d\tau}}$$

The wavefunction $N\psi$ is also called as the **Normalized Wave Function**. In future when ever we write ψ without any further specifications, we will assume that it has been normalized.

- The same reasoning implies that $\int | \psi |^2 d\tau = 1$ implies that ψ cannot be zero everywhere since in that case $| \psi |^2 d\tau = 0$ everywhere and $\int | \psi |^2 d\tau = 0$ but the particle has to be present somewhere!

- ψ must be **Single Valued**. If in any region ψ has more than one value then in that region $| \psi |^2 d\tau$ has more than one value. This means that in a particular region there may be different probabilities of finding the particle - a ridiculous proposition!

- ψ cannot be infinite anywhere, since then $\int | \psi |^2 d\tau = \infty$. Suppose we try to normalize this, then N must be zero! Or in other words, $N^2| \psi |^2 d\tau$ would be zero everywhere except where its value is infinity. This is unacceptable.

To summarize, the normalised wave function ψ must be continuous with a continuous slope. It must also be single valued and finite. It also cannot have zero value everywhere.

With all these restrictions it is clear that the equation $H\psi = E\psi$ cannot have an acceptable solution ψ for any arbitrary value of energy E. Thus, only certain values are acceptable for a particle. In other words, this means that the energy of a particle is QUANTIZED.

The Quantum Mechanical Principles

Let us now develop a quantitative and broad understanding of the quantum mechanical principles, terms and concepts without getting any details of mathematics.

The equation $H\psi = E\psi$ is called an Eigen equation. Eigen means 'self' in German. **H** is an Eigrn operator, **E** is an eigen value of the operator H. ψ is an eigen function corresponding to the eigen value E and is different for different eigen values.

textbfH is called the Hamiltonian operator also known as the energy operator, since by operating on a particular eigen function ψ we get the value (the precise value) of the energy of the particle in a state represented by ψ.

In equation (1) we had the operator $H = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$. The quantity **H** is an OPERATOR, something that carries out an operation on the function ψ. In this it means that we multiply ψ by $\frac{\hbar^2}{2m}$ and take its second derivative and add the results to V(x) multiplied by ψ. As a result we get a constant **E** multiplied by ψ where **E** is the enrgy of the particle in a state represented by ψ,

An example of an eigen function of an eigen operator is $\psi = e^{ax}$ is an eigen function of the eigen operator $\frac{\partial}{\partial x}$ since $\frac{\partial \psi}{\partial x} = \frac{\partial}{\partial x}(e^{ax}) = ae^{ax} = a\psi$ or $\frac{\partial}{\partial x}(e^{ax}) = a(e^{ax})$ or $\frac{\partial}{\partial x}(]psi) = a(\psi)$

In terms of physical interpretation ψ contains all information regarding the motion and position of the particle it represents. **H** is an operator corresponding to the observable **E** (Energy). In general for any operator corresponding to an observable (a measurable property) we can use the Schrödinger equations. We can in general write,

(operator corresponding to an observable)(wavefunction) = (value of the observable)(wavefunction)

Thus, if we knew both the wave function ψ and the operator say $\hat{\Omega}$ corresponding to the observable ω of interest, and the wavefunction is an eigenfunction of the operator $\hat{\Omega}$, then we can predict the outcome of an observation of the property Ω (ex. an atoms energy) by picking out the ω in the eigen value equation,

$$\hat{\Omega}\psi = \omega\psi$$

Superposition and Expectation values

The problem however is that when the wave function is not the eigen function of an operator, then the corresponding property (corresponding to the operator) does not have a definite value. The techniques used is to construct or write the wave function as a linear superposition of eigenfunctions of the operator.

Suppose ψ_1, ψ_2, ψ_3 ... are eigen functions of the momentum operator $\hat{\Omega}$, then we may write the following,

$$\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + ... = \sum_k c_k\psi_k$$

Then according to Quantum Mechanics,

- When the momentum is measured, in a single observation one of the values corresponding to the ψ_k that contribute to the superposition will be found.

- Which of these is possible, values will be found is unpredictable. However the probability of finding a particular value (say ω_k corresponding to the eigen function ψ_k) in a series of observations is proportional to the square modulus of its coefficients in the superposition ($\mid c_k \mid^2$).

- The average value of a large number of observations is given by the expectation value $< \Omega >$ of the operator $\hat{\Omega}$. This expectation value is defined as

$$< \Omega >= \int \psi^*\hat{\Omega}d\tau$$

The Uncertainity Principle

It has been shown that is we precisely specify the momentum of a particle, the expectation value of the position of the probability becomes independent of position,

i.e. the particle has equal probability of existing anywhere. This means that "If the momentum is specified precisely, it is impossible to predict the location of the particle." It may also be shown that the opposite is also true, i.e. "If the position of a particle is precisely determined specified, then the momentum of the particle cannot be predicted."

The Heisenberg's uncertainity principle states, "It is not possible to specify simultaneously, and accurately, both the momentum and the position of a particle."

Quantitatively, if Δ p is the uncertainty in the momentum and Δ x is the uncertainity in the position of the particle in any simultaneous determination then $\Delta p * \Delta x \geq \frac{h}{4\pi} or \frac{\hbar}{2}$.