Introduction to Quantum Mechanics

Classical Mechanics: Since Newton, physical description of a single particle is based on the notions of coordinates, momenta and trajectories. Physical state of a point-like particle is fully defined if the position is known and the momentum is known at the same time. If these two parameters are known at time zero (t=0) then one can use the Newton equation, F=ma, to calculate the trajectory of the particle. Here *m* is the mass of the particle, *F* is the force acting on the particle and *a* is its acceleration. The acceleration is calculated by taking the derivative of the velocity with respect to the coordinate of the particle,

$a=dv/dx$

The velocity is the derivative of the position (the coordinate) with respect to time, i.e.,

$v=dx/dt$

The force, *F*, is calculated from the potential energy of the particle by taking its derivative with respect to the particle coordinate:

$F=-dU/dx$

Thus, one can solve the second-order differential equation

$$m\frac{d^2x}{dt^2} = -\frac{dU}{dx}$$

and calculate the trajectory of the particle at any time in the future as well as in the past. One needs to know the "state" of the particle at some moment in time, say at *t=0*. **The "state" of the particle is defined by two numbers, its position *x* and its momentum *p=mv*.** To use classical mechanics for the prediction of the future states of the particle (i.e., to calculate its trajectory) one needs to know also the potential energy of the particle as a function of the particle position, *U(x)*.

Classical Mechanics: Hamiltonian method: The kinetic energy of the particle is $K=mv^2/2=p^2/2m$. The total energy is $E=K+U$. The total energy is sometimes called the Hamiltonian., H. so we can write:

$H=K+U=p^2/2m+U(x)$

The motion (the trajectory) can be described by two Hamilton equations:

$$\frac{dp}{dt} = -\frac{\partial H}{\partial x}$$

$$\frac{dx}{dt} = \frac{\partial H}{\partial p}$$

The equation are written in terms of partial derivatives, which means that if the derivative is taken with respect to x then p is assumed constant and if the derivative is taken with respect to p then x is assumed constant, etc.

Exercise: check that the two Hamilton equation are equivalent to the Newton equation F=ma.

The key concept for the transition to the quantum mechanics (QM) is the notion of the sate of the particle. In classical mechanics (CM) the state is defined as a set of two numbers, x and p. It is in principle possible to perform an experiment, a measurement of the particle state at any moment in time. If the measurement device is well designed then we will get the result predicted by the Newton equations, which is of course equivalent to the prediction of the Hamilton equations.

We will see that in the context of quantum mechanics it is not enough to specify two numbers. One need to specify a function of coordinates at each moment of time. This function we call the wave function, It provides the most complete description of the state of the particle. Such description based on the idea that each quantum particle (say, an electron) has properties analogous to a wave. And, as is well know, to describe a wave one needs to specify a function in space. Such function defines the shape of the wave, whatever the shape is. The square of the wave function also defines the energy density for an electromagnetic wave for example, or the density of photons.

Quantum Mechanics (QM): Planck's formula: Quantum mechanics was introduced by Heisenberg (Nobel prize 1932 "for the creation of quantum mechanics, the application of which has, inter alia, led to the discovery of the allotropic forms of hydrogen"). This theory is mathematically rather complicated and involves matrices and operator; will see some elements of it. One key ingredients for the quantum theory, namely the idea of the energy quantization, was envisioned by Planck already in 1900. According to the Planck's formula, the energy is emitted is discrete quanta, and one quantum of energy is defined as $E = hf$, where h is just a constant (Planck's constant) and f is the frequency of the emitted wave (for example, an electromagnetic wave). The value of the Planck's constant is $h=6.62607015 \times 10^{-34}$Js.

For example, if one makes a pendulum or a harmonic oscillator of any sort and manages to measure the smallest energy it can absorb, that energy will be $E = hf$, where f is the oscillation frequency. The formula is applicable to any wave or any sort of oscillator. *But everything is made of harmonic oscillators!*

This same rule of thumb applies even to electronic devices, for example to LC-circuits. If one connects a capacitor and an inductor in parallel, the circuit can support harmonic oscillations. The energy is quantized in units *hf*, where f is the frequency of the LC-contour. Light waves also, when emitted by an excited atom, for example, are emitted as energy quanta, called photons. Each photon carrier the energy defined by Planck's formula as well, *E=hf*.

Note that the wavelength, λ, of the wave and its frequency are related to each other as $\lambda f=c$, where c is the speed of the wave (called phase velocity). One can also introduce the period T=1/f. Then $\lambda=c/f=cT$. In other words, the wavelength is the distance the wave travels within one period of its oscillation.

Quantum Mechanics (QM): de Broglie waves:

Another key idea in QM, introduced by De Broglie, is that the particles of matter, such as electrons or protons, behave as waves, the wavelength being $\lambda = \frac{h}{p}$. Here $p=mv$ is the momentum of the particle. This formula can be understood qualitatively if we remember that for any wave of period T we have $\lambda = Tv$, where v is the wave velocity. And, according to Planck, $E=hf=h/T$. Thus, $\lambda = Tv = hv/E$. For high energy particles, for which v is approaching the speed of light, c, the energy, approximately, is $E=pc$. Thus, if we replace v with c, we get $\lambda = hc/pc = h/p$. De Broglie proposed that this equation is more general and applies in all cases.

These two key ideas (i.e., E=hf and $\lambda = h/p$) can be combined into one formula if we ascribe a wave (called "wave function") $\Psi(x,t) = \cos(kx - \omega t) = \cos(px/\hbar - Et/\hbar)$ to the particle. For now, for simplicity, we assume this is a real valued function. Later we will see that the wave function in QM needs to be a complex-valued function.

Here $k = p/\hbar = \frac{h}{\lambda \hbar} = \frac{2\pi}{\lambda}$ is so-called "wave number". (It is also called "wave vector" if the particle propagates in 2 or 3 dimensions.) The reduced Planck's constant is $\hbar = \frac{h}{2\pi}$. The angular frequency of the wave is related to the energy of the particle as follows $\omega = E/\hbar$. Such wave function satisfies both conditions: the wavelength is defined by the momentum and the frequency is defined by the energy. This wavefunction is the most important mathematical tool to describe the state of the particle with a well-defined momentum and well-defined energy. If we would measure the momentum of such particle we always get the "p" value and if we measure the energy, we always get the "E" value. But if we would measure the position, we would get a random unpredictable number since the wave spreads from minus infinity to plus infinity on the x-axis.

Although the wave function approach are well established in quantum physics, and provide an accurate description of various quantum system, the physical meaning of these waves remains somewhat mysterious to this day. Yet, all known alternatives are basically equivalent to the wave function approach. Thus, to describe quantum particles mathematically we have to understand how to handle such wave functions.

Quantum Mechanics (QM): Superposition: Let us discuss the meaning of the wavefunction $\Psi(x, t)$. We are looking to describe a particle mathematically. The wavefunction provides a complete description of the quantum state of the particle. All measurable physical quantities can be derived from the wavefunction (by using operators which we will discuss later). Based on our classical physics understanding, the physical state of particle is described by a trajectory, x(t), not but by any sort of "wave". The wave function description, on the other hand, is related to another big idea in QM, the idea of quantum superposition. The principle of superposition states that if a physical state named "A" is a possible state of a particle and some state "B" is another possible state of the particle then the particle can also exist in both states simultaneously. For a classical particle such superposition is not possible. In classical physics, if a particle is located at a position x=1, for example, then it cannot be located at a different position x=2, at the same time. But quantum particles can do this because they behave as waves and waves can superimpose. For example, a light wave can contain two or many colors. And each color is a different wave function. Mathematically speaking, a superposition is possible because the equation describing the waves (the Schrodinger equation, see below) is linear. Thus, any combination of two true solutions is a true solution also.

Quantum Mechanics (QM): Probabilistic interpretation of the wave function: The wavefunction is the distribution of the probability amplitudes for different possible locations of the particle. The square of the absolute value of the wavefunction equals the probability density: $\rho(x,t) = |\Psi(x,t)|^2$. So, if we know the wavefunction and we measure the location of the particle then the probability that the particle is found in the interval between x and $x+dx$ equals

$$\rho(x,t)dx = |\Psi(x,t)|^2\,dx$$

To better understand why such interpretation of the wave function makes sense consider the following example.

Consider electromagnetic field (EM field), e.g., light waves. The energy density of the EM field is B^2/μ, where μ is the magnetic permeability and B is the magnetic field of the electromagnetic wave. On the other hand, the energy density is the density, ρ, of the corresponding particles (photons) multiplied by the energy E_1 stored in one particle, i.e., $B^2/\mu = \rho E_1$. The particles or the quanta of energy composing the EM field are called photons. As was previously discussed, the energy of one photon is defined by the frequency, f, of the corresponding wave, $E_1 = hf$. Thus, the energy density of the electromagnetic field is $B^2/\mu = \rho hf$. From this, the density of the photons is $\rho = B^2/\mu hf$. The wave in this example is describe by the deviation of the magnetic field from its equilibrium value, which is zero. Thus, we see how the density of particles is proportional to the wave function squared , $B^2(x,t)$.

But what if there is only one particle? In this case, quantum mechanics tells us that the particle is located in multiple places of space at the same time. In other words, the particle does not have a definite location. We can only calculate the probability to find the particle at various locations. (Fluorescent screens can be used to measure locations of photons or electrons, for example.) This probability naturally is represented by the same function ρ, which was the density of particles in cases when many particles were present. To summarize: if there are many particles then one can calculate the average number of particle in a volume V_0 as $N_0 = \int_{V_0} \rho(x)dV$, and if there is only one particle then the probability to detect this particle in a volume V_0 is given by the same formula $N_0 = \int_{V_0} \rho(x)dV$. In both cases $\rho(x,t)dx = |\Psi(x,t)|^2\,dx$

Quantum Mechanics (QM): Probabilistic interpretation of the wave function: So, the "state" of the particle is described by a wave of probabilities (probability amplitudes, to be more precise), and not by trajectories, like in classical physics. Before the position is measured the particle "does not know" where it is located. In some sense it is everywhere, i.e., in all points where the wavefunction is not zero.

The fact that a single quantum particle (say, one electron) behaves as a wave can be tested experimentally. For this one needs to send electrons at a screen with two holes. Behind this screen a fluorescent screen is placed, which can visualize the location of the arriving particles. In this setting, one observes interference fringes on the second screen, as one would expect for waves passing through two holes and then interfering. This interference happens even one sends particles on a one-by-one basis, which proves that each particle interference with itself. Or, to be more precise, each all possible trajectories of the particle interference with each other.

If the system under consideration contains not just one but many particles, all having the same wavefunction, then the wavefunction (its absolute value squared, to be more precise) represents the density of particles, i.e., the number of particles per unit volume. In such case the probability density is replaced by the average density. In this way we transition from individual particles to a field of particles. For example, one can visualize that when many photons are coherently superimposed one gets an electromagnetic wave of a large amplitude.

Quantum Mechanics (QM): Phenomenology:

Now, if we apply the definition given above to a cosine wave, we gat a probability which is modulated in space. Yet, in the simplest case, the probability should be equal everywhere. Or, for a flux of many particles, the flux density and the energy density are constant, in the simplest case of a uniform beam. To achieve constant flux and constant probability density $\rho(x,t)$ we need to introduce complex valued functions.

Imaginary unit is called "i". It is defined as the root of the equation $y^2=-1$. The solution of such equation is denoted either "i" or "-i". Thus, we can write one solution as y=i and the second solution is y=-i. (For more details see: https://en.wikipedia.org/wiki/Imaginary_unit). Any complex number can be written as z=a+ib, where a and b are real numbers. We also need to introduce so-called complex-conjugate numbers, which are defined as z*=a-ib. Then zz*=(a+ib)(a-ib)=a^2+b^2 is always a real number. This formula defines the magnitude squared of z.

The Euler formula is needed also: $e^{i\omega t} = \cos(\omega t) + i\sin(\omega t)$ or, in a more general format, $e^{i(kx-\omega t)} = \cos(kx - \omega t) + i\sin(kx - \omega t)$. The $e^{i(kx-\omega t)}$ function is called "plane wave" wave function.

Rom the Math prospective, the real-valued cosine and sine waves can be compiled as (check this by yourself):

$$\cos(kx - \omega t) = \frac{1}{2}\left[e^{i(kx-\omega t)} + \left(e^{i(kx-\omega t)}\right)^*\right] = \frac{1}{2}\left[e^{i(kx-\omega t)} + e^{-i(kx-\omega t)}\right]$$

$$\sin(kx - \omega t) = \frac{1}{2i}\left[e^{i(kx-\omega t)} - \left(e^{-i(kx-\omega t)}\right)^*\right] = \frac{1}{2i}\left[e^{i(kx-\omega t)} + e^{-i(kx-\omega t)}\right]$$

Quantum Mechanics (QM): Phenomenology: The wavefunction of a plane wave is $\Psi(x,t) = e^{i(kx-\omega t)}$, where k=p/ $\hbar$ and ω =E/ $\hbar$.

In physics, we want to calculate physical quantities and then measure them. The question now is: how do we calculate the momentum of a plane wave.

In quantum theory we use operators. Each physical quantity has an operator. For example, the **momentum operator** is: $\hat{p} = -i\hbar\dfrac{\partial}{\partial x}$

General rule: If the operator is applied to the wavefunction then we get the same wavefunction multiplied by the corresponding physical quantity, if and only if this physical quantity has a well defined value in the quantum state considered.

Suppose we have a quantum state which wavefunction is a plane wave. Let us see what the **momentum operator** will do to this wavefunction:

$\hat{p}\,\Psi = \hat{p}\,e^{i(kx-\omega t)} = -i\hbar\dfrac{\partial}{\partial x}e^{i(kx-\omega t)} = \hbar k\,e^{i(kx-\omega t)} = p\,e^{i(kx-\omega t)}$

So, we get the result as expected: upon application of the momentum operator to the wavefunction one gets the same wavefunction multiplied by the momentum, p. Such quantum state is called an eigenstate of the momentum operator. Note that in such description x and t are variables and p and k and E and ω are assumed constant numbers. This is why such representation is called "coordinate representation".

Conclusion: In quantum mechanics (QM), physical quantities are represented by operators. There exist physical states in which a given quantity has a definite value. Such state is called an eigenstate of the corresponding operator. The main practical property of the eigenstates is that if one measures the corresponding physical quantity then one always gets the same value. In this respect QM is not probabilistic. The occurrence of probabilities and uncertainties occurs because quantum particles can be in superpositions of many different eigenstates.

For example one can design a wave function out of states with different momenta:

$$\Psi(x, t) = e^{i(k_1 x - \omega_1 t)} + e^{i(k_2 x - \omega_2 t)}$$

In such cases a single measurement will give an unpredictable result.

Quantum Mechanics (QM): Phenomenology:

The conclusion given above can be presented mathematically as follows. Suppose we consider some physical quantity A. It would always have a corresponding operator $\hat{A}$. The eigenstates are defined by the following eigenequation: $\hat{A}\psi_0 = A_0 \psi_0$

In this case ψ_0 is the eigenstate of the particle. Suppose we prepare our particle in this state ψ_0. Then we measure the quantity A. Then the result will always be A_0.

Suppose we prepare the system in a different eigenstate, ψ_1. Now we measure the physical quantity A. Then the result of the measurement is a different value, say A_1. Again, everything is predictable. There is no uncertainty in this scenario.

Let us now remember about superposition principle. We can prepare the system in a linear combination of the two states. Assume we prepare the system in a state $\psi_0 + \psi_1$. Now we measure the quantity A. The result is 50% chance to get A_0 and 50% chance to get A_1. In this situation there is no way to predict the outcome with certainty. Yet even in this case we can say with certainty that such measurement of the physical quantity A will produce either the outcome A_0 or the outcome A_1, but not some different value.

Why unpredictability happens?

Because the newly constructed state is not an eigenstate. One can see this as follows:

$$\hat{A}(\psi_0 + \psi_1) = A_0 \psi_0 + A_1 \psi_1 \neq const * (\psi_0 + \psi_1)$$

Example: the energy operator is called Hamiltonian, *H*. The energy is defined as the kinetic energy, $p^2/2m$, plus potential energy V(x). So, the Hamiltonian operator is

$$\widehat{H} = \frac{\widehat{p}^2}{2m} + V(\widehat{x})$$

Notice how we use known operators of the momentum and the position of the particle, to construct the new operator, the Hamiltonian. This is how new operators are constructed in general. Now, we need to remember that the position operator is just a multiplication of the wavefunction by the variable x, i.e.,

$\widehat{x}\psi_0 = x\, \psi_0$ for any wavefunction.

The Hamiltonian acting on a wavefunction gives the following change of the wave function: $\widehat{H}\psi = \frac{\widehat{p}^2}{2m}\psi + V(\widehat{x})$

$\psi = \frac{1}{2m}\left(-i\hbar\frac{\partial}{\partial x}\right)^2 \psi + V(x)\,\psi$

Quantum Mechanics (QM): Phenomenology:

Time-dependent Schrodinger equation: $i\hbar \frac{\partial}{\partial t}\Psi = \hat{H}\Psi$

Typically, we use the low-case $\psi(x)$ to denote the time-independent wavefunction and the capital $\Psi(x,t)$ to denote the wave function which changes in time.

Let us assume that the energy of a quantum particle has a definite value. This means that if we perform an experiment and measure the energy then we will get a predetermined value, say E_1. the corresponding quantum state of the particle is Ψ_1. Since the energy is well defined therefore it is the eigenstate of the Hamiltonian.

Therefore: $\hat{H}\Psi_1 = E_1\Psi_1$ This is called time-independent Schrodinger equation.

So, the time-dependent Schrodinger equation becomes:

$i\hbar \frac{d}{dt}\Psi_1 = \hat{H}\Psi_1 = E_1\Psi_1$

The solution for this quantum state (quantum state #1) is therefore $\Psi_1(x,t) = \psi_1(x)e^{-\frac{iE_1 t}{\hbar}}$

If a is localized, like electron in the hydrogen atom is localized around the nucleus, then the quantum states can be numbered. They form a discrete spectrum. The spectrum is calculated using the time-independent Schrodinger equation:

$\hat{H}\Psi_n = E_n\Psi_n$

Note that n here represent integer numbers which are used to number the states of the electron in which its energy has a definite value.