Concepts of Chemistry for Engineering
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Lecture No. 03
Laws of quantum mechanics

In our quest to find an answer to the question, what everything is made up off, we have reached a situation where we have understood that a deterministic theory is not going to work. What we really need, a probabilistic theory, something that might sound a little counterintuitive to start with. Well, when I say little that is an understatement, it sounded very, very counterintuitive.

And so, things like what you see here, God rolling dice, these are things that were sort of inspired in spheres beyond the scientific one. And Einstein eventually made this very famous statement, where he said God does not play dice. I encourage you to find out what Stephen Hawking had said about this statement of Einstein. But this God rolling dice is something that nicely depicts the situation of the debate that was going on about quantum mechanics at the time.

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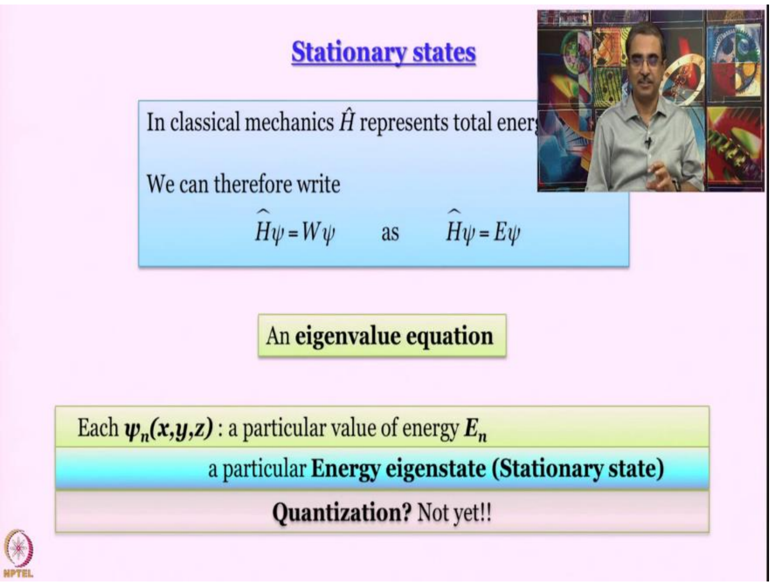

Stationary states

In classical mechanics $\hat{H}$ represents total ener

We can therefore write

$$\hat{H}\psi = W\psi \qquad \text{as} \qquad \hat{H}\psi = E\psi$$

An **eigenvalue equation**

Each $\boldsymbol{\psi_n(x,y,z)}$: a particular value of energy $\boldsymbol{E_n}$

a particular **Energy eigenstate (Stationary state)**

Quantization? Not yet!!

Where are we, we were here, we found out that stationary states can be described by wave function and we can extract the value of energy of the stationary state by making the Hamiltonian operate on the wave function. So, we get an eigenvalue equation, what does it mean? Wave function knows what the particular value of energy is, you ask it and it will tell you what is the energy of the system. The question is how do you ask it? You ask it by making the Hamiltonian operator the total energy operator operate on it.

And how does it give the answer? It gives the answer in the form of an eigenvalue, energy eigenvalue here, that is why we say that each ψ is a particular energy eigenstate. And it is worthwhile to remember that we do not have quantization yet, what we have is that this understanding that as far as energy is concerned, knows what the energy is and you can formulate an eigenvalue equation by using the total energy operator operating on ψ to give you the value of the energy as the eigenvalue. From here, the postulates of quantum mechanics were formulated.

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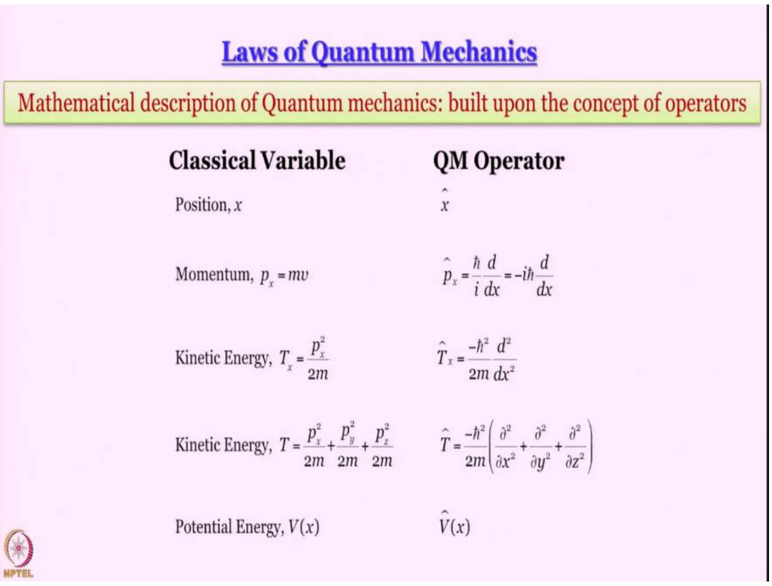

Laws of Quantum Mechanics

Mathematical description of Quantum mechanics: built upon the concept of operators

Classical Variable	QM Operator
Position, x	$\hat{x}$
Momentum, $p_x = mv$	$\hat{p}_x = \frac{\hbar}{i}\frac{d}{dx} = -i\hbar\frac{d}{dx}$
Kinetic Energy, $T_x = \frac{p_x^2}{2m}$	$\hat{T}_x = \frac{-\hbar^2}{2m}\frac{d^2}{dx^2}$
Kinetic Energy, $T = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m}$	$\hat{T} = \frac{-\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right)$
Potential Energy, $V(x)$	$\hat{V}(x)$

Here we have called them laws of quantum mechanics. So, the first postulate is that wave function contains the information about not the energy, but possibly about everything, there should be some wave function that contains the information about whatever physical observable that we are looking for.

And correspondingly, there must be an operator for each and every physical observable, and these operators were worked out, again operator algebra is something that was developed by that time that was used in this context and these are the operators some quantum mechanical operators that you see for different classical variables.

If you want to find out momentum, the operator that you have to use is $\frac{\hbar}{i}\frac{d}{dx}$, if you want to find out kinetic energy, well, this is not very difficult to understand $\frac{p_x^2}{2m}$. So. $-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2}$ just remember the meaning of $\frac{\partial^2}{\partial x^2}$ is $\frac{\partial}{\partial x}$ operating twice, you have something ψ, you find first derivative with respect to dx, then find second derivative that is basically square of operator, square of operator means same operator operating twice in succession. So, so on and so forth, you can build an operator for each and every classical variable.

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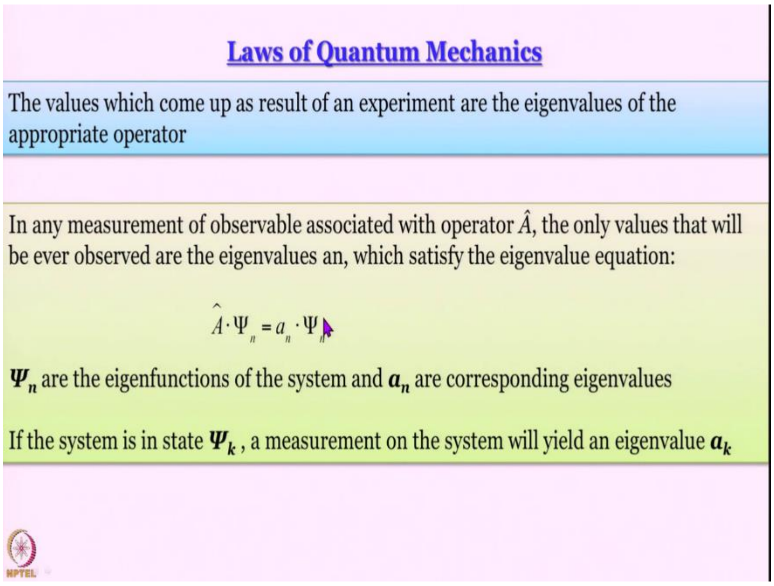

Laws of Quantum Mechanics

The values which come up as result of an experiment are the eigenvalues of the appropriate operator

In any measurement of observable associated with operator $\hat{A}$, the only values that will be ever observed are the eigenvalues an, which satisfy the eigenvalue equation:

$$\hat{A}\cdot\Psi_n = a_n\cdot\Psi_n$$

$\boldsymbol{\Psi_n}$ are the eigenfunctions of the system and $\boldsymbol{a_n}$ are corresponding eigenvalues

If the system is in state $\boldsymbol{\Psi_k}$, a measurement on the system will yield an eigenvalue $\boldsymbol{a_k}$

And then like what we saw in Schrodinger equation, the values that come up as a result of experiment they are essentially eigenvalues of the appropriate operator, Â operating on Ψ_n gives you a_n multiplied Ψ_n, so these are the very basic postulates.

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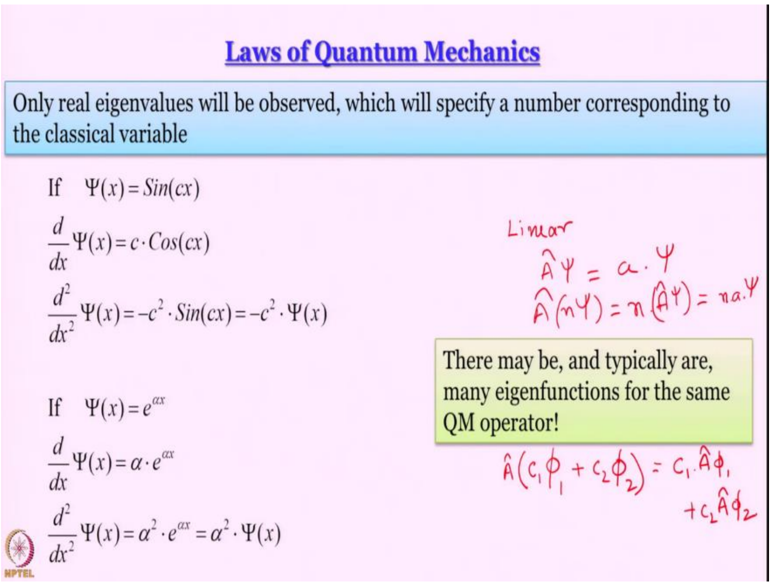

Laws of Quantum Mechanics

Only real eigenvalues will be observed, which will specify a number corresponding to the classical variable

If $\Psi(x) = Sin(cx)$

$$\frac{d}{dx}\Psi(x) = c\cdot Cos(cx)$$

$$\frac{d^2}{dx^2}\Psi(x) = -c^2\cdot Sin(cx) = -c^2\cdot\Psi(x)$$

If $\Psi(x) = e^{\alpha x}$

$$\frac{d}{dx}\Psi(x) = \alpha\cdot e^{\alpha x}$$

$$\frac{d^2}{dx^2}\Psi(x) = \alpha^2\cdot e^{\alpha x} = \alpha^2\cdot\Psi(x)$$

Linear

$$\hat{A}\Psi = a\cdot\Psi$$

$$\hat{A}(n\Psi) = n(\hat{A}\Psi) = na\cdot\Psi$$

There may be, and typically are, many eigenfunctions for the same QM operator!

$$\hat{A}(c_1\phi_1 + c_2\phi_2) = c_1\cdot\hat{A}\phi_1 + c_2\hat{A}\phi_2$$

And then, we have some interesting inferences from there also. See, eigenvalues have to be real. If I want to know the momentum, can my momentum be e^{imx}? No, momentum has to be a real number. It is a real quantity So, I can only use operators that are what are called Hermitian,

Hermitian means the eigenvalue Hermitian operators always have real eigenvalues. There is something called turnover rule and on we do not have to go into that in this course.

So, many Eigenfunctions can be possible for a quantum mechanical operator. One more thing that I have not written here is that the quantum mechanical operators are also linear. What does that mean? If Â operates on say Ψ to give me 'a' multiplied by Ψ, then you simply multiply n by Ψ, multiply Ψ by n, what will happen Â will operate on this to give me n multiplied by Â.Ψ , that is n.a.Ψ.

Another way of writing this is Â operates on some C_1 coefficient multiplied by ϕ_1, see I do not necessarily have to write Ψ for wave function, I can write whatever I want. So, I will write ϕ here, plus C_2 operating on ϕ_2, that will be $C_1.\hat{A}.\phi_1 + C_2.\hat{A}.\phi_2$. So, the operators have to be linear as well, this comes from the postulates.

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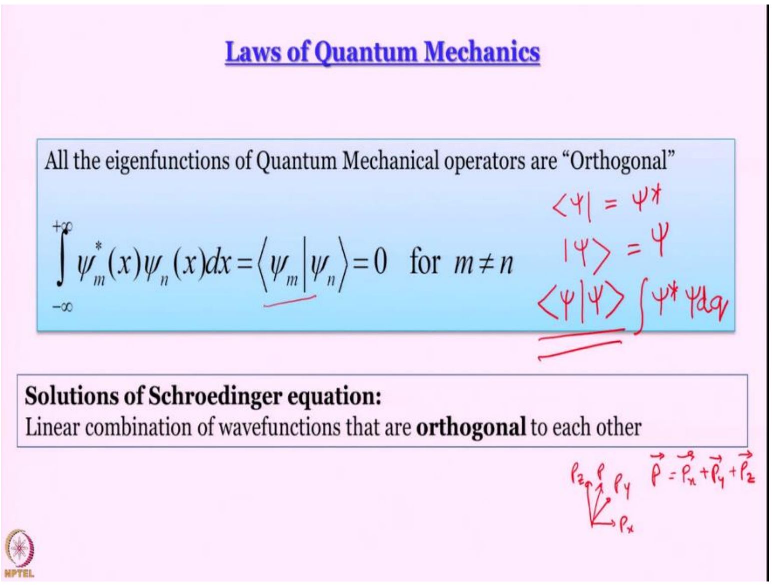

Laws of Quantum Mechanics

All the eigenfunctions of Quantum Mechanical operators are "Orthogonal"

$$\int_{-\infty}^{+\infty} \psi_m^*(x)\psi_n(x)dx = \langle \underline{\psi_m} | \psi_n \rangle = 0 \quad \text{for } m \neq n$$

$\langle \Psi | = \Psi^*$

$| \Psi \rangle = \Psi$

$\underline{\langle \Psi | \Psi \rangle} \int \Psi^* \Psi dq$

Solutions of Schroedinger equation:
Linear combination of wavefunctions that are **orthogonal** to each other

$\vec{P} = \vec{P_x} + \vec{P_y} + \vec{P_z}$

Another thing is all eigenfunctions of quantum mechanical operators are orthogonal. In fact, it is I like to say that solutions of Schrodinger equations are such that they are actually linear combinations of wave functions that are orthogonal to each other. What does that mean? What it means is that the solutions are all in some kind of a function space. What is the meaning of function space? Let us say I am talking about momentum, I have Px, I have Py, I have Pz.

So, if I have a momentum, any momentum P, it is not very difficult for you to see that, P here is a vector isn't? So, it is not very difficult for us to see that this P is really a vector sum of Px +Py + Pz. So, in P space, momentum space, I can write any momentum as a linear combination of the orthogonal mutually orthogonal of Px, Py and Pz, orthogonal means they do not have components around each other.

So, similarly, any wave function can be written as a linear sum of a set of wave functions that are orthogonal to each other. And orthogonality means this, essentially it is the same condition as condition for orthogonality of vectors. But it is written a little more perhaps intimidating form, $\int_{-\infty}^{+\infty} \Psi_m^*(x)\Psi_n(x)dx$=0. And this notation,$\langle\Psi_m|\Psi_n\rangle$ is something that we will use again and again. So, let me just write what it is, this is called Dirac's Bracket notation.

In this notation, this $<|$ vector is called the Bra vector and if I write Ψ in it, then ideally mean Ψ^*, the vector facing opposite, $|>$ this is called the Ket vector. If I write Ψ in a Ket vector, I mean just Ψ. But when you join them up, I get something more than just $\Psi^*\Psi$. If I write like this $<\Psi\ |\ |\ \Psi>$ or $<\Psi|\Psi>$, then what I mean is this $<\Psi\ |$ will be Ψ^*, $|\ \Psi>$ will be Ψ.

But when you write in the bracket, when you combine Bra and Ket, it really means that I am integrating over the entire range of whatever coordinate it is in terms of which the wave functions are written. So, we are going to use this bracket notation very often because it is easier to draw angular brackets rather than this curly integral signs. Jokes apart, it makes things a little easier. So, solutions of Schrodinger equation are really linear combination of wave functions that are orthogonal to each other.

So, these are the ground rules or postulates of quantum mechanics that we are going to use. Now, with this what we what are we saying, we are saying that, to know the value of any observable, the only coordinate we have to be honest, is only variable we have is Ψ, and Ψ tells us what is the property when you make a measurement, and when you make a measurement, let us see the property has a value P.

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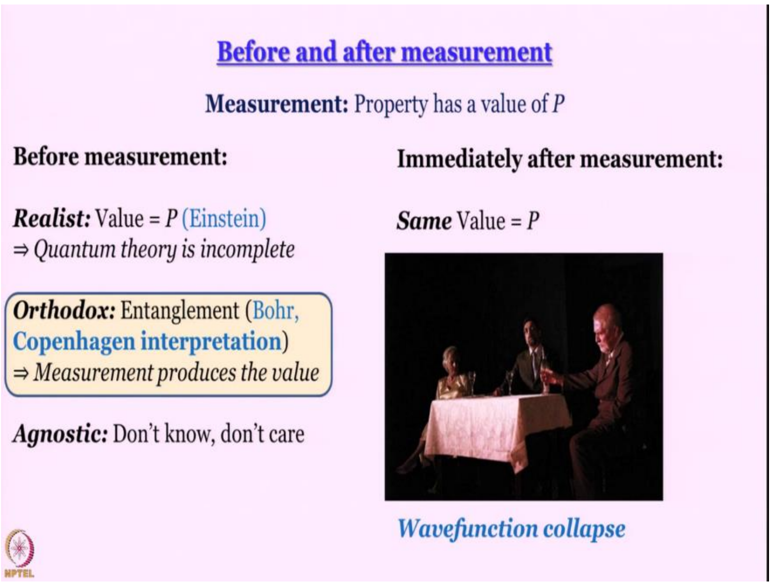

Before and after measurement

Measurement: Property has a value of P

Before measurement:

Realist: Value = P (Einstein)
⇒ *Quantum theory is incomplete*

Orthodox: Entanglement (Bohr, **Copenhagen interpretation**)
⇒ *Measurement produces the value*

Agnostic: Don't know, don't care

Immediately after measurement:

Same Value = P

Wavefunction collapse

Now, this sort of philosophical question that was asked was that what happens before you make the measurement? Is the property P or is it something else? And Einstein and a group of scientists who supported him believed that, that value has to be P, this is called the realist view. Come on you measure, it is P immediately before what value would it have been it has to be P, nothing else. Then the question is why can we not measure it?

He said we cannot measure it because the theory is not complete. See, Bohr theory you had n principal quantum number with that you could not explain line structure, you could not explain Zeeman Effect. So, to explain it further, you have to bring in more coordinates. So, to speak quantum numbers in another way we can call them coordinates, if you had to bring in the coordinate l, coordinate m, to account for a spin you had to bring in s.

So, realist view as quantum mechanical formulation of Schrodinger is not complete and Ψ is not the only thing, if you bring in something else, you will be able to say what it was before the measurement. But, orthodox view by Bohr and Heisenberg and a lot of other scientists this is also called Copenhagen interpretation, orthodox view said that you cannot measure. Before measurement according to orthodox view, the system exists in an entangled state.

So, it is very important to understand the difference between the realist and the orthodox view, they agree more or less that we have not been able to say what the value is before the measurement. The difference is the realist view says that the value is P, it is just that your theory is not complete. So, you could not measure, orthodox view says the theory is complete, it is in-determinate, not measurable like $\Delta x.\Delta p_x \geq \frac{h}{4\pi}$.

That is not because of any shortcoming of the instrument, it is a natural threshold. Here also they are saying nature is such that the system exists in entangled state you cannot really tell what is n, what is l, nothing you can say nothing. Only when you make the measurement, you understand what the state is in and not only that, depending on what measurement you do, the system is created in that particular way. The property of the observable is determined by the property of the observer.

Of course, there is this agnostic view, which says we do not know and we do not care. How does it matter, let us work with what we are doing? And that is actually an easy way of not thinking too much. But then, what has happened is that this debate has gone on for 30 years. Only in 1965, Thomas Bell did some experiment to prove conclusively that the orthodox view is correct and realist view is not correct.

Whoever is interested in learning a little more about this, I recommend to you the book on Quantum Mechanics by Griffiths. So, if you read it, you will, this issue is discussed in chapter 1 and the last chapter. So, we will not be able to go that far in this course, but suffice to say that it is the orthodox view that is now accepted. And we will make occasional references to this orthodox view as we go along in this course. But now, this is such a mind-boggling question that it has enthralled audiences again, beyond the scientific community for ages.

So, there is this fantastic play called Copenhagen, which I had the good fortune to see Tom Walter had brought it to IIT Bombay a few years ago, when he was alive. This is all about a discussion between Bohr and Heisenberg. Fantastic play if you get a chance to see it, please do see it. So, now, what we are saying is that we do not really, we cannot really determine what it was before the measurement, what everybody agrees upon is that what happens after the measurement.

If you make a second measurement immediately after the first one, then you are going to see the same value P. Why? Because now the wave function has collapsed into an eigenfunction and the eigenfunction which has yielded the eigenvalue that you have observed. This, I am not surprised, if you find this discussion to be a little abstract and overwhelming. I just wanted to introduce this, we do not claim that we have solved all the answers, the purpose is to raise the question and make you aware of this really big issue that has traveled the best minds mankind has ever produced over many, many decades.

This is a fascinating field to study, we will refer to this sometimes, but do not worry at this point, if you have not understood all of what we have said in a really in a nutshell. So, that is what it is fine. We have lived to the fact whether we understand this Copenhagen interpretation or not, what we have lived up to the fact is that wave function contains the information about the system, if you use an appropriate operator, then it yields the value of physically observable, physical observables. And that is what you can observe experimentally as well.

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But what is this wavefunction?

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But the nagging question that comes back to haunt us is, what is this wave function? I mean, everything is made up of waves. What does it mean? We do not see waves around. This answer came from the interpretation provided by Max Born. That is what we will discuss in the next module.