Fundamental of Spectroscopy

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Lecture – 03
Introduction to Quantum Mechanics – II

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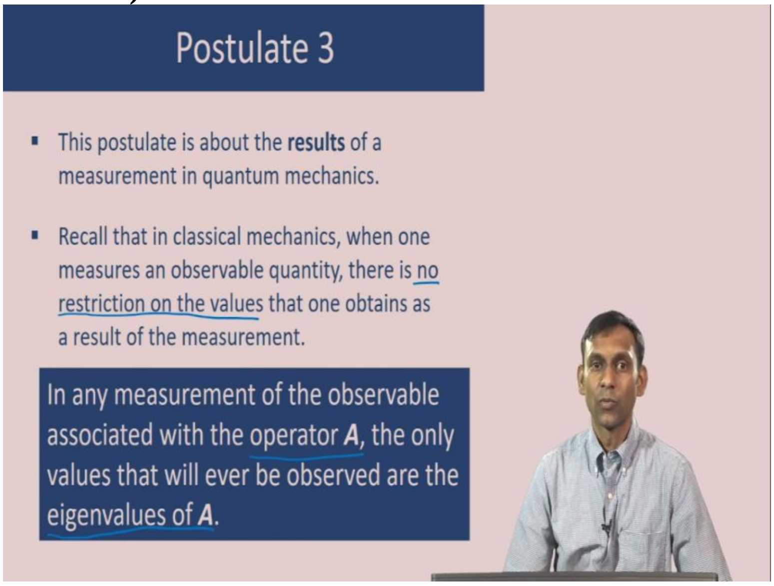

Postulate 3

- This postulate is about the **results** of a measurement in quantum mechanics.
- Recall that in classical mechanics, when one measures an observable quantity, there is no restriction on the values that one obtains as a result of the measurement.

In any measurement of the observable associated with the operator ***A***, the only values that will ever be observed are the eigenvalues of ***A***.

In the last lecture, I mentioned that we will study quantum mechanics by studying 5 postulates, we have looked at 2 postulates so far. So, let us now look at the third postulate. This postulate is about the results of a measurement in quantum mechanics. Recall that in classical mechanics, if one measures an observable quantity, Let us say we measure energy of a particle, we can get any possible value of that energy. There is no restriction on the values that one obtains when one mixer measurement on a classical particle.

However, that is different in quantum mechanics. And that is what postulate 3 is about. So the statement of postulate 3 is that in any measurement of an observable which has the associated operator A the only values that 1 will ever obtain are the eigenvalues of A. So, let us look at what eigenvalues mean and what 1 can get when you make a measurement on A.

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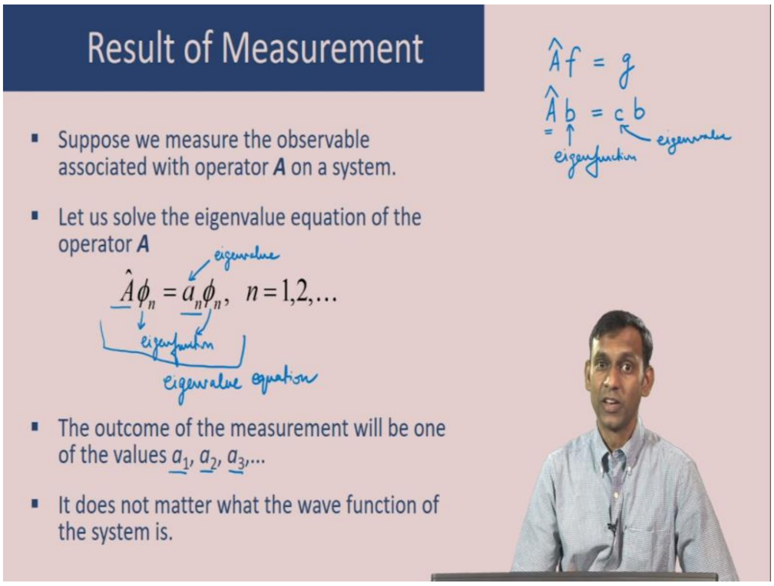

Result of Measurement

- Suppose we measure the observable associated with operator ***A*** on a system.
- Let us solve the eigenvalue equation of the operator ***A***

eigenvalue

$$\hat{A}\phi_n = a_n\phi_n, \quad n=1,2,\ldots$$

eigenfunction

eigenvalue equation

- The outcome of the measurement will be one of the values $a_1, a_2, a_3, \ldots$
- It does not matter what the wave function of the system is.

$\hat{A}f = g$

$\hat{A}b = cb$

eigenfunction

eigenvalue

So, the eigenvalues of A are these constants here. Let us examine that. So, suppose you have an operator A in general, when that acts on function f you get another function g. However, there are certain functions, which when you operate with the operator A for example, let us say the function b, then you get a constant times b then this function b is called an eigenfunction of A .

And this constant here is called the eigenvalue corresponding to the eigenfunction b. So, all functions are certainly not eigenfunctions of an operator, let us say A, but the ones that are that satisfy the equation written here are called eigenfunctions. So, coming back to the measurement of the observable corresponding to the operator A, you see here that we have solved the eigenvalue equation of the operator A.

These phi are the eigenfunctions and this constant A is the eigenvalues and you see of course, that there are multiple eigenvalues and eigenfunctions denoted by n = 1, 2 and so on. Now, the postulate states that when we make a measurement, the outcome of the measurement will be 1 of these values a 1, a 2, a 3 and so on. So, you cannot get any value like in classical mechanics, there is a restriction on the values that you can get.

And in particular, the values that you can get our eigenvalues of the operator A. The equation that you see here is called the eigenvalue equation of A. So, you solve the eigenvalue equation of A and that tells you what possible values you can get when you measure the observable corresponding to A. Now, note here that it does not matter what the wave function of the system is.

It just depends on the operator. So, if you are measuring the energy, the eigenvalue corresponding to energy or what you can measure, when you make a measurement of energy on the system, it does not depend on what the wave function of the system is. But the wave function as we have seen contains all information about the system. In particular, it will tell us which eigenvalue is obtained when you make the measurement.

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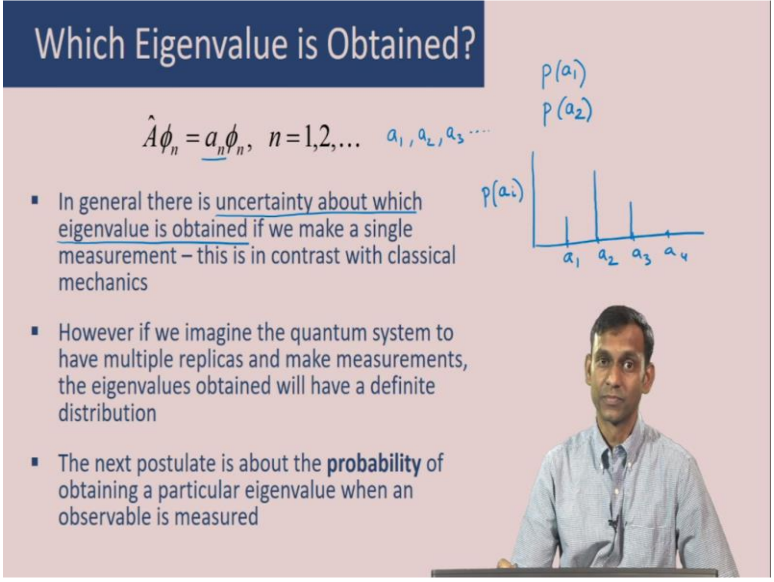

Which Eigenvalue is Obtained?

$$\hat{A}\phi_n = a_n\phi_n, \quad n = 1,2,\ldots$$

- In general there is uncertainty about which eigenvalue is obtained if we make a single measurement – this is in contrast with classical mechanics
- However if we imagine the quantum system to have multiple replicas and make measurements, the eigenvalues obtained will have a definite distribution
- The next postulate is about the **probability** of obtaining a particular eigenvalue when an observable is measured

So, let us look into that question now. So, here we have rewritten the eigenvalue equation again and the eigenvalues of the operator are a 1 a 2 a 3 and so on. The question is which eigenvalue is actually obtained when you measure a. In general there is uncertainty about which eigenvalue is obtained if we make a single measurement on a single classical system. Now, this of course, is not contrast with classical mechanics.

Where if you have multiple replicas of an identical system, then when you go and measure a property, you will get the same value of that property when you make a measurement on 2 identical systems. This is different in quantum mechanics. And therefore, quantum mechanics is very non intuitive, that even when you have identical systems, or if you imagine identical replicas of a system, and you make measurements on those systems.

You can actually get different eigenvalues when you make a measurement. So, there is uncertainty about which eigenvalue is obtained. However, even though these eigenvalues would be different in these multiple replicas, there is something which is certain and that is that these eigenvalues have very definitive probability for occurring. So, for example, if you call the probability of obtaining eigenvalue a as p of a 1.

Probability of obtaining eigenvalue as p of a 2 these probabilities have a distribution. So if you plot this, and you write eigenvalue a 1, a 2, a 3, a 4 and so on this axis, and on this axis, you plot the probability of obtaining a certain eigenvalue, let us say a i, then it could be that a 1 has this probability a 2 has that probability a 3 has a certain different probability a 4 might have 0 probability and so on.

This information is contained in the wave function. And this distribution of eigenvalues is absolutely definite. So, although the result of each individual measurement is uncertain, and is not definite, when we make a large number of measurements on multiple replicas, then the distribution of probabilities of each eigenvalue is completely definite. That is what the next postulate is about. It tells us what this distribution of probability will be.

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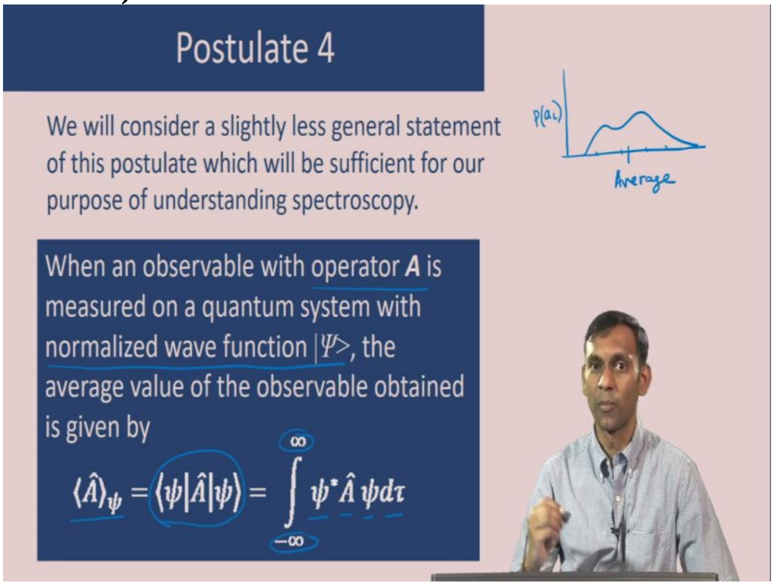

Postulate 4

We will consider a slightly less general statement of this postulate which will be sufficient for our purpose of understanding spectroscopy.

When an observable with operator ***A*** is measured on a quantum system with normalized wave function |Ψ>, the average value of the observable obtained is given by

$$\langle \hat{A} \rangle_\psi = \langle \psi | \hat{A} | \psi \rangle = \int_{-\infty}^{\infty} \psi^* \hat{A} \psi d\tau$$

So, let us look at postulate 4 let me mention that we will consider a slightly less general statement of this postulate in this course, because that will be sufficient for our purpose of understanding spectroscopy and it will save us from some more complicated mathematics. So, the statement that we will consider as postulate 4 is that, when we make a measurement of the observable corresponding to the operator A.

And the wave function of the quantum system is represented by the normalized wave function psi then the average value of the observable obtained is given by the integral here, which is psi star A psi d tau integrated from - infinity to infinity, which in shorthand notation is written like this, the Dirac notation which we have seen before in the previous lecture, or you know the notation which denotes average, which is here on the left side.

The point is that the wave function contains information about the probability of every individual eigenvalue. So, you could have a distribution of eigenvalues and this could be how the distribution looks like of the different eigenvalues. Now, the wave function contains the information about what these different probabilities are but we will restrict ourselves to only know what the average value of this distribution is. And that is what this form of postulate 4 is telling us.

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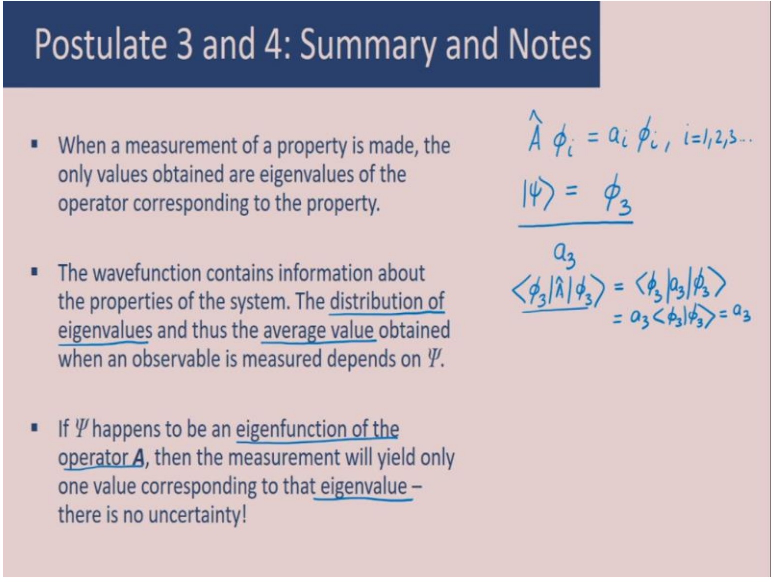

Postulate 3 and 4: Summary and Notes

- When a measurement of a property is made, the only values obtained are eigenvalues of the operator corresponding to the property.
- The wavefunction contains information about the properties of the system. The distribution of eigenvalues and thus the average value obtained when an observable is measured depends on *Ψ*.
- If *Ψ* happens to be an eigenfunction of the operator ***A***, then the measurement will yield only one value corresponding to that eigenvalue – there is no uncertainty!

$$\hat{A}\phi_i = a_i\phi_i, \quad i=1,2,3\ldots$$

$$|\psi\rangle = \phi_3$$

$$\overset{a_3}{\langle\phi_3|\hat{A}|\phi_3\rangle} = \langle\phi_3|a_3|\phi_3\rangle$$

$$= a_3\langle\phi_3|\phi_3\rangle = a_3$$

To summarize postulate 3 and 4, when a measurement of a property is made on a quantum system, the only values obtained are eigenvalues of the operator corresponding to the property we are measuring. The wave function contains information about the properties of the system. In particular, it tells us what the distributions of eigenvalues are and therefore, what the average value of the property is.

The postulate tells us what this average value of a particular property is. So, again if you measure let us say energy of a quantum particles it will tell you what the average value of that energy is the energy itself might have different values and it would have a distribution. postulate 4 tells us what that average value is. If psi happens to be an eigenfunction of the operator A.

Then the measurement will yield only 1 value corresponding to the eigenvalue in that case, there is no uncertainty let us understand this. So, if you have the operator A and let us say phi i is an eigenfunction with eigenvalue a i. Now, suppose the wave function of the system is happens to be some phi 3 here the eigenfunctions of the operator or let us say phi i = 1 2 3 and so on.

Now, suppose the wave function of the system happens to be phi 3, then if you make a measurement of the property A on the system with a function phi 3, the eigenvalue that you will get or the result of the measurement that you will get is a 3 and only a 3. So the average value which is returned as phi 3 a phi 3 will be phi 3 a 3, which is a constant time phi 3, this constant comes out of the integral.

So you have a 3 phi 3 phi 3 and because phi 3 is normalized this is simply equal to a 3. So, the average value is simply a constant in this case, and every time you make a measurement of the property a on this system, you are going to get the value a 3 interestingly this average value that we have been talking about is sometimes referred to as expectation value. Now, these are just synonyms.

And average value is the more accurate term, because when you make a measurement, you expect to get a distribution of values not this average value, but because of convention, the average value is also referred to as expectation value and it is a commonly accepted terminology.

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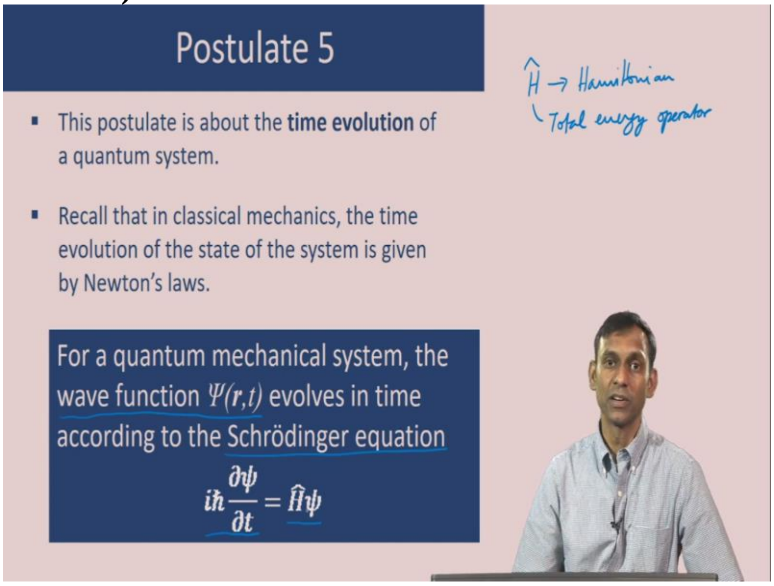

Postulate 5

- This postulate is about the **time evolution** of a quantum system.
- Recall that in classical mechanics, the time evolution of the state of the system is given by Newton's laws.

For a quantum mechanical system, the wave function $\Psi(r,t)$ evolves in time according to the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = \hat{H}\psi$$

$\hat{H} \rightarrow$ Hamiltonian

Total energy operator

Let us know look at postulate 5. This postulate tells us about the time evolution of a quantum system. Recall that in classical mechanics, the time evolution of the position and the momentum of a particle are given by Newton's laws in quantum mechanics, the time evolution of the state of the system or the wave function which is a function of position and time is given by the Schrodinger equation.

Which is the following here i h bar del psi / del t = H psi H as we have talked about before is the Hamiltonian operator which corresponds to the total energy, the kinetic energy and the potential energy. So, this is the total energy operator. So, we can see that the Hamiltonian operator is particularly important for quantum mechanics, it tells us how this wave function evolves in time.

The left hand side of this equation is the first derivative with respect to time and the right hand side is the Hamiltonian operating on the wave function.

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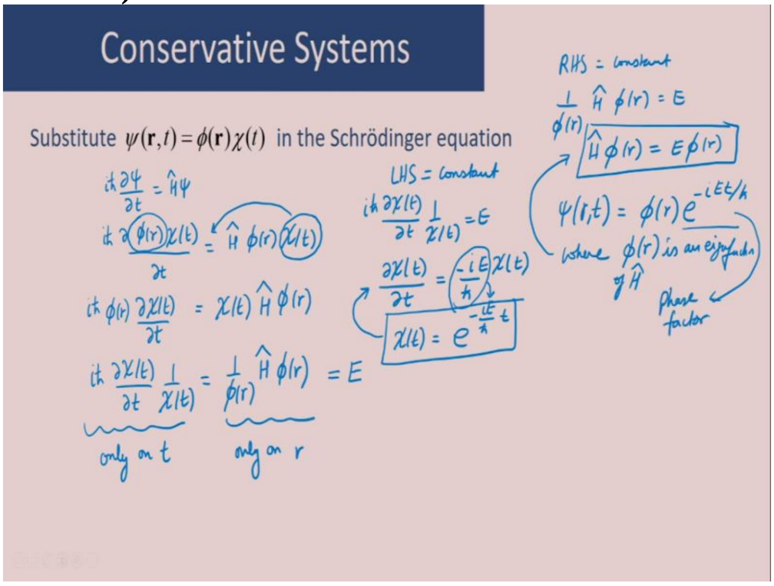

Conservative Systems

Substitute $\psi(\mathbf{r},t)=\phi(\mathbf{r})\chi(t)$ in the Schrödinger equation

$$i\hbar\frac{\partial\psi}{\partial t}=\hat{H}\psi$$

$$i\hbar\frac{\partial\,\phi(r)\chi(t)}{\partial t}=\hat{H}\,\phi(r)\chi(t)$$

$$i\hbar\,\phi(r)\frac{\partial\chi(t)}{\partial t}=\chi(t)\,\hat{H}\phi(r)$$

$$\underbrace{i\hbar\frac{\partial\chi(t)}{\partial t}\frac{1}{\chi(t)}}_{\text{only on } t}=\underbrace{\frac{1}{\phi(r)}\hat{H}\phi(r)}_{\text{only on } r}=E$$

LHS = Constant

$$i\hbar\frac{\partial\chi(t)}{\partial t}\frac{1}{\chi(t)}=E$$

$$\frac{\partial\chi(t)}{\partial t}=\frac{-iE}{\hbar}\chi(t)$$

$$\boxed{\chi(t)=e^{-\frac{iE}{\hbar}t}}$$

RHS = Constant

$$\frac{1}{\phi(r)}\hat{H}\phi(r)=E$$

$$\boxed{\hat{H}\phi(r)=E\phi(r)}$$

$$\psi(r,t)=\phi(r)e^{-iEt/\hbar}$$

where $\phi(r)$ is an eigenfunction of $\hat{H}$

Phase factor

Let us consider a special case which will be particularly important in the study of chemistry, this is the case when the Hamiltonian does not depend on time. These systems are called conservative systems, because you can show that in this case the average energy of the system does not change with time. So, 4 systems where the Hamiltonian is, time independent, let us see how the wave function evolves in time.

Let us try the following special form of the wave function here and see whether it is a solution. So, the special form is that this wave function which is a function of position and time is written as a function of only position and multiplied by a function of only time. Let us substitute this into the Schrodinger equation and see whether this can be possible solution. So, substituting this in the Schrodinger equation, we get my i h bar del psi / del t = H psi.

That is the Schrodinger equation and if I substitute I get i h bar del phi r chi t / del t = H of phi r chi of t. Now, you notice that the function phi of r depends only on the position and therefore, this derivative of time does not operate on it. So, you can take the phi r out of this derivative and write this as i h bar phi r del chi t / del t on the right hand side the Hamiltonian does not depend on time.

So, this function which is a function of only time chi of t can be taken out and move to the left like this and you get chi t = H of phi of r. Now, we collect parts with the same variable on each side. So, on the left hand side let us collect terms which are functions of time. So, chi t / del t, 1 over chi t on the left side, and on the right hand side, we have 1 over phi of r H of phi of r.

Now you notice that the left hand side of this equation depends only on time and the right hand side depends only on position now, the position and time are 2 independent variables, they will vary independent of each other and not be connected. So, for this equation to be true where one part depends only on time and the other part depends only on position. The only way that this can be satisfied at all times is if these individual parts.

The left hand side and the right hand side are both constants. So, let us say they equal to a constant which we will call each. Now, let us see what we get by equating the left hand side and the right hand side separately to this constant E. if we consider the left hand side equal to a constant we get i h bar del chi t / del t, 1 over K of t = E and this is del del chi t / del t = - i / h bar E of chi t.

This is now a first order ordinary differential equation, where you have a function chi, which when you take a first derivative gives you a constant times the function chi. Now, you know that a particular solution of this can be chi of t = e to the power of - i E / h bar t. So, you have this constant here multiplied by t, this will be a solution of this equation and you can very easily check by substituting it back into this equation.

If you substitute the solution here on the left hand side, you will get the right hand side. So, here is the solution which works for this equation. Now, if you take the right hand side to be constant we get 1 over phi r H of phi r = E which is saying that any phi r which is an eigenfunction of the Hamiltonian, you see this year that will satisfy the original Schrodinger equation.

So, a solution of the Schrodinger equation psi of phi r, t = phi of r multiplied by e to the power of - i Et / h bar were phi of r is an eigenfunction of H that is this statement and you have the time part which is just here, which is sometimes called a phase factor.

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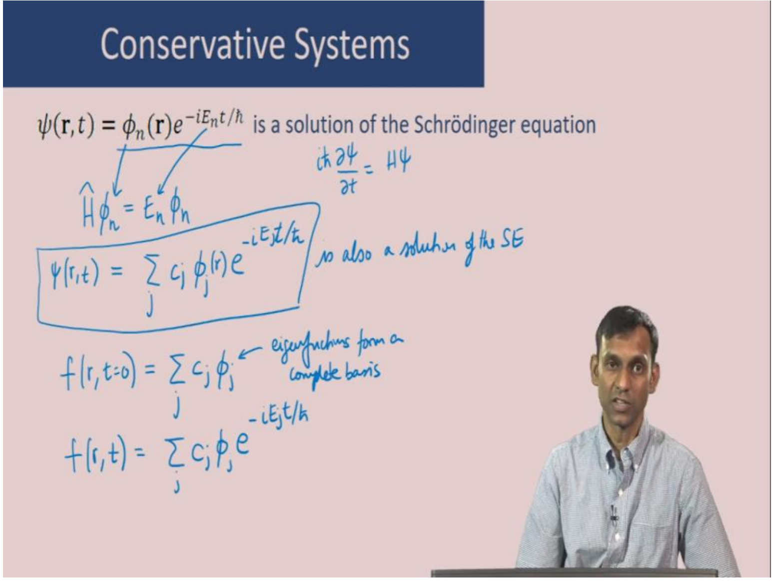

Conservative Systems

$\psi(\mathbf{r},t) = \phi_n(\mathbf{r})e^{-iE_nt/\hbar}$ is a solution of the Schrödinger equation

$i\hbar\frac{\partial\psi}{\partial t} = H\psi$

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

$\boxed{\psi(r,t) = \sum_j c_j \phi_j(r) e^{-iE_jt/\hbar}}$ is also a solution of the SE

$f(r,t=0) = \sum_j c_j \phi_j$ ← eigenfunctions form a complete basis

$f(r,t) = \sum_j c_j \phi_j e^{-iE_jt/\hbar}$

We have seen that the following form of the wave function is a solution of the Schrodinger equation i h bar del psi / del t = H psi when the Hamiltonian does not depend on time. So, here these phi are just eigenfunctions of the time independent Hamiltonian and the E is the corresponding eigenvalue so, here is the eigenfunction and this E is the eigenvalue. Now, you can very easily show that a wave function of the form phi r , t.

Which is a linear combination of the following form j C j phi jof r, e to the power of - i E j t / h bar is all also a solution of the Schrodinger equation. I have used the variable j instead of i, because there is a i here which corresponds to the imaginary number i. So just to avoid confusion I have used E j. Now, this result that wave function of this form is a solution is a fairly powerful result.

Because it gives you a way, to write the time evolution of any general wave function. For example, let us say are the wave function at a time t = 0 for a system is f of r. Now, you can write this wave function as a linear combination of the eigenfunctions of the Hamiltonian, because we have seen in postulate 2 that the eigenfunctions form a complete basis then the time evolution of this wave function is really simple.

Because you have f of r time t, you have to take this linear combination and just add the appropriate phase factors like this. We have seen that this will be a solution of the Schrodinger equation.

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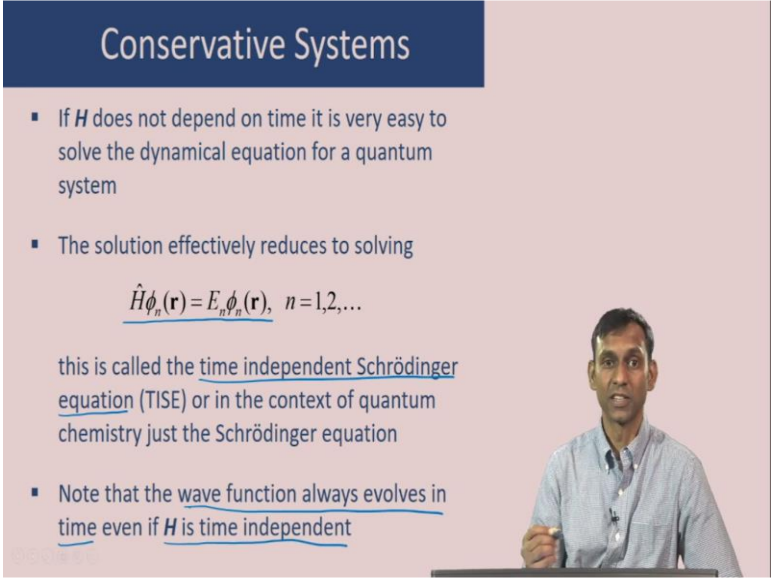

Conservative Systems

- If H does not depend on time it is very easy to solve the dynamical equation for a quantum system
- The solution effectively reduces to solving

$$\underline{\hat{H}\phi_n(\mathbf{r}) = E_n\phi_n(\mathbf{r})}, \quad n = 1,2,\ldots$$

this is called the time independent Schrödinger equation (TISE) or in the context of quantum chemistry just the Schrödinger equation

- Note that the wave function always evolves in time even if H is time independent

So, if H does not depend on time, it is very easy to solve the dynamical equation for a quantum system. The solution effectively reduces to solving an eigenvalue equation for the time independent Hamiltonian. This eigenvalue equation is called the time independent Schrodinger equation and sometimes in the context of quantum chemistry, this equation is just called the Schrodinger equation.

So, you have to know whether Schrodinger equation refers to this equation or whether it refers to the dynamical equation just based on context. Note that the wave function always evolves in time even if the Hamiltonian is time independent, the wave function evolves in time.

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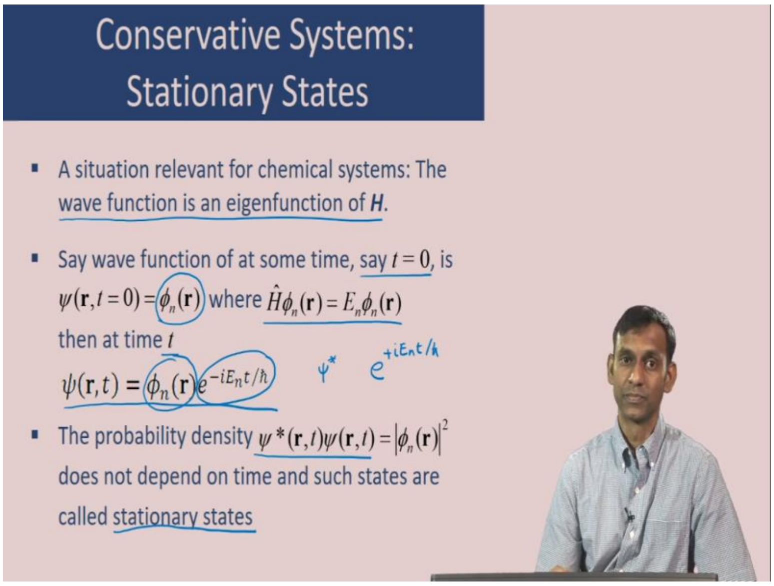

Conservative Systems:
Stationary States

- A situation relevant for chemical systems: The wave function is an eigenfunction of ***H***.
- Say wave function of at some time, say $t = 0$, is $\psi(\mathbf{r}, t = 0) = \phi_n(\mathbf{r})$ where $\hat{H}\phi_n(\mathbf{r}) = E_n\phi_n(\mathbf{r})$ then at time t

$$\psi(\mathbf{r}, t) = \phi_n(\mathbf{r})e^{-iE_nt/\hbar} \qquad \psi^* \qquad e^{+iE_nt/\hbar}$$

- The probability density $\psi^*(\mathbf{r}, t)\psi(\mathbf{r}, t) = |\phi_n(\mathbf{r})|^2$ does not depend on time and such states are called stationary states

We will now look at a further special case of conservative systems. This is the situation When the wave function is an eigenfunction of the Hamiltonian and it is a very relevant situation for chemical systems know if the wave function at some time say time t = 0 has this eigenfunction phi of phi n of r where this phi n is an Eigen satisfies the eigenvalue equation of the Hamiltonian.

Then we have seen that at time t, the wave function has the following form. So, it is the wave function at time t = 0 multiplied by the phase factor which tells you what this wave function will be at a future time t. Now the probability density in this case very interestingly psi star psi does not depend on time and that is because when you take complex conjugate psi star, the time part becomes e to the power of + I E n t / h bar.

And that cancels with the time part in psi and this wave function becomes independent of time. Because this probability density does not depend on time, such states are called stationary states, we will use the idea of stationary states throughout this class. The other property of stationary states is that, if we make a measurement of a property, which has an observable, which is time independent. Then we get the same value at all times, the property measurement does not depend on time.

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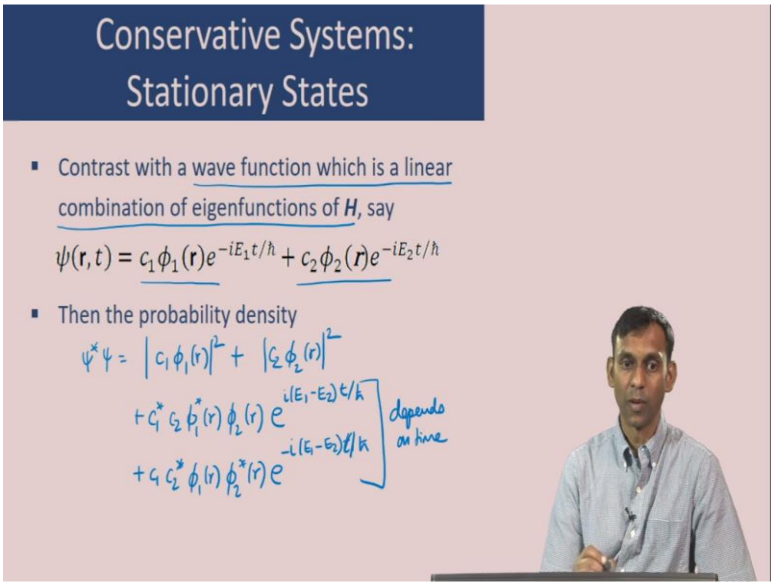

Conservative Systems: Stationary States

- Contrast with a wave function which is a linear combination of eigenfunctions of ***H***, say
  $\psi(\mathrm{r},t) = \underline{c_1\phi_1(\mathrm{r})}e^{-iE_1t/\hbar} + \underline{c_2\phi_2(r)}e^{-iE_2t/\hbar}$
- Then the probability density

$$\psi^*\psi = |c_1\phi_1(r)|^2 + |c_2\phi_2(r)|^2 \left.\begin{aligned} &+ c_1^* c_2 \phi_1^*(r)\phi_2(r)e^{i(E_1-E_2)t/\hbar} \\ &+ c_1 c_2^* \phi_1(r)\phi_2^*(r)e^{-i(E_1-E_2)t/\hbar} \end{aligned}\right] \text{depends on time}$$

We can contrast this with a situation where the wave function is not an eigenfunction of the Hamiltonian, but a linear combination of eigenfunctions of the Hamiltonian. Let us say we take a simple situation where it is a linear combination of 2 eigenfunctions phi 1 and phi 2 then the probability density looks like chi star chi psi = c 1 phi 1 r square + c 2 phi 2 r square + the cross terms.

c star c 2 phi 1 star r phi 2 r e to the power of i E 1 - E 2 t / h bar + c 1 c 2 star phi 1 r phi 2 star r e to the power of – i E 1 – E 2 t / h bar we can see here that the probability density does depend on time. Unlike the situation where, in the case of stationary states, the probability density did not depend on time.