Statistical Mechanics
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Lecture - 41
Quantum Statistical Mechanics Density Matrix

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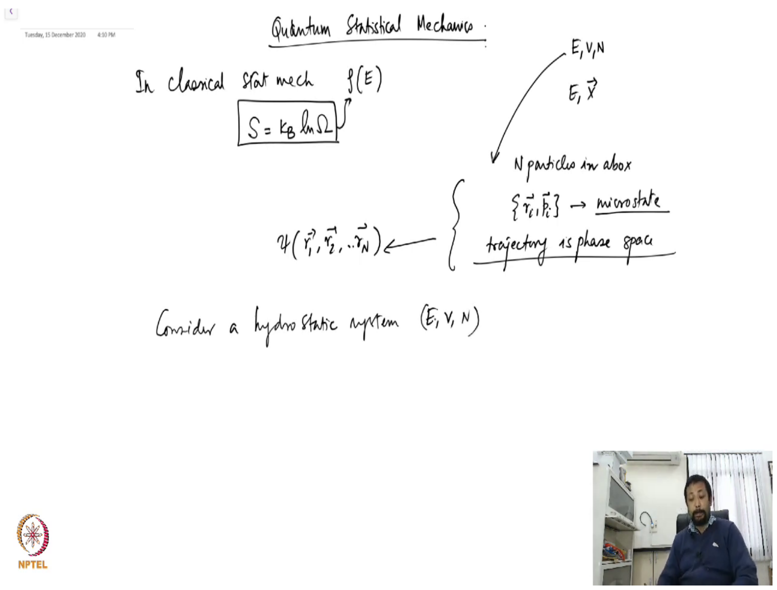

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Quantum Statistical Mechanics

In classical stat mech $\rho(E)$

$\boxed{S = k_B \ln \Omega}$

E, V, N

$E, \vec{X}$

N particles in a box

$\{\vec{r}_i, \vec{p}_i\} \rightarrow$ microstate

trajectory is phase space

$\psi(\vec{r}_1, \vec{r}_2, \ldots \vec{r}_N) \leftarrow$

Consider a hydrostatic system (E, V, N)

Welcome back. So, in this lecture our focus is going to be on Quantum Statistical Mechanics. In classical stat mech we had already derived an expression for the probability of being in the micro state with an energy E, right. And, in classical stat mech we also realize that essentially for a given macro state which is characterized by E, V and N for a hydrostatic system.

And, more generally E and X, where X denotes a generalized coordinates they will rise an infinite possible number of microstates. And, from the basic in the from the foundation of first principle of statistical mechanics that is identifying the entropy K B as ln times omega we could derive the probability density of the system being in a microstate with an energy E, right.

But, in quantum stat mech things are little different. For a hydrostatic system if you take N particles in a box then the classical stat mech I know that r i and p i the set of coordinates and the momenta form a microstate. But, in quantum stat mech we cannot have such an identification because it is not possible to simultaneously measure the coordinates and the momenta.

Further whereas, we had a trajectory in phase space in a classical stat mech in the classical picture this is replaced in quantum mechanics, this is replaced by a wave function.

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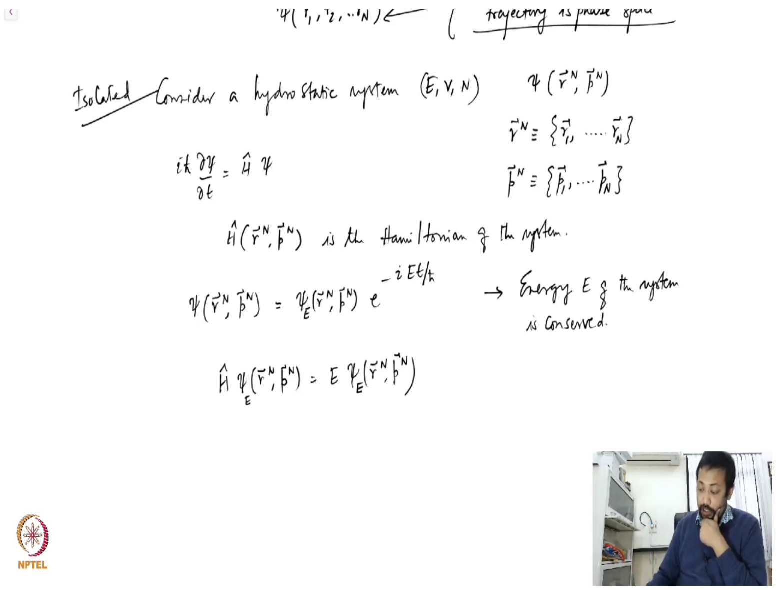

$\Psi(r_1, r_2, \ldots r_N) \leftarrow$ (trajectory in phase space

~~Isolated~~ Consider a hydrostatic system (E, V, N) $\qquad \Psi(\vec{r}^N, \vec{p}^N)$

$\vec{r}^N \equiv \{\vec{r}_1, \ldots \vec{r}_N\}$

$\vec{p}^N \equiv \{\vec{p}_1, \ldots \vec{p}_N\}$

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

$\hat{H}(\vec{r}^N, \vec{p}^N)$ is the Hamiltonian of the system.

$$\Psi(\vec{r}^N, \vec{p}^N) = \Psi_E(\vec{r}^N, \vec{p}^N)\, e^{-iEt/\hbar}$$

$\rightarrow$ Energy E of the system is conserved.

$$\hat{H}\, \Psi_E(\vec{r}^N, \vec{p}^N) = E\, \Psi_E(\vec{r}^N, \vec{p}^N)$$

Now, consider a hydrostatic system with the macroscopic variables E, V and N right. The wave function of this system is denoted by where r N is the set r 1, r N and this defines the set of momenta of these particles.

This is an isolated system we right. We will consider it to be an isolated system and the evolution of the wave function follows a Schrodinger equation which is well known to all of you is given by H hat psi, where H hat is also a function of r N, p N is the Hamiltonian of the system.

The evolution the time evolution of this I can solve this equation and I can simply write it down is equal to psi of r N, p N E to the power minus E t over H bar because the energy E of the system is conserved so that the time independent Schrodinger equation base. So, this is the eigenvalue of the energy equation. So, you write it down as E times psi of r N, p N right.

So, one has to identify that this is the eigen function of the energy and therefore, this becomes the eigen function of the energy.

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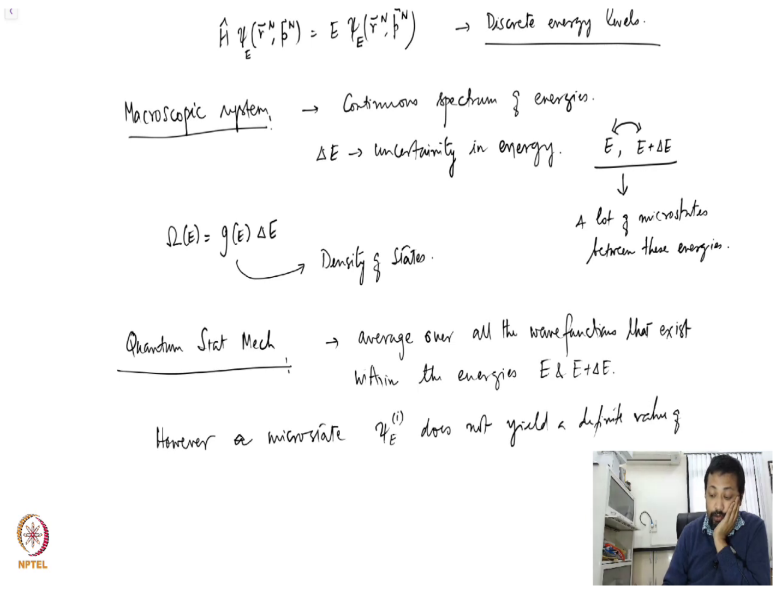

$$\hat{H}\,\psi_E(\vec{r}^N;\vec{p}^N) = E\,\psi_E(\vec{r}^N;\vec{p}^N) \rightarrow \underline{\text{Discrete energy levels.}}$$

Macroscopic system → Continuous spectrum of energies.

ΔE → uncertainity in energy. $\underline{E,\ E+\Delta E}$ ↓ A lot of microstates between these energies.

$\Omega(E) = g(E)\,\Delta E$ → Density of States.

Quantum Stat Mech → average over all the wavefunctions that exist within the energies E & $E+\Delta E$.

However a microstate $\psi_E^{(i)}$ does not yield a definite value of

Now, typically the solutions might have discrete energy levels. So, this can have discrete energy levels if you consider one particle or two particle systems. However, if you are considering a macroscopic system if you are considering a macroscopic system with a large number of degrees of freedom, then the difference between the respective energy levels is discrete energy levels decreases and you have a continuous spectrum of energies.

There are often degeneracy’s also and for a given energy therefore, you can have a more than one wave function, right. So, it is also worth noting that in a microscopic system it is not always possible to know the exact values of the energies. So, you can always allow for a certain uncertainty delta E in your energy, just as we had allowed in the classical case.

So, essentially you are looking at an energy between E and E plus delta E, right and there exists a lot of microstates between these two energies. So, the micro canonical ensemble in quantum systems in quantum stat mech is essentially counting these number of microstates that lies between the two energy levels E N E plus delta E. So, we will write down O omega E as g E times delta E where this function that we have is essentially known as the density of states.

Now, therefore, in quantum mechanics or rather saying that in quantum stat mech instead of averaging of a all the phase points that we did in the classical case, what we do is we average over all the wave functions that exist within and energy within the energies E and E plus delta E.

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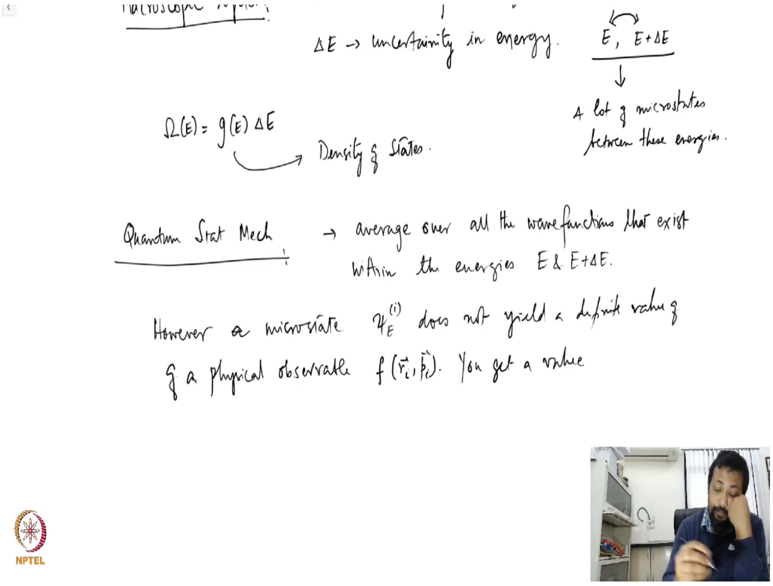

$\Delta E \rightarrow$ uncertainity in energy.

$\overline{E,\ E+\Delta E}$ $\downarrow$ A lot of microstates between these energies.

$\Omega(E) = g(E)\,\Delta E$ $\rightarrow$ Density of States.

Quantum Stat Mech $\rightarrow$ average over all the wavefunctions that exist within the energies E & $E+\Delta E$.

However a microstate $\psi_E^{(i)}$ does not yield a definite value of a physical observable $f(\vec{r}_i, \vec{p}_i)$. You get a value

However, one should note very very carefully that if you are measuring that if you are measuring. However, a micro state psi i E of or let us say we will just denote it as psi I E does not yield a definite value of a physical observer, right. And, let us say we denote that observable as r i p i rather what you get is you get an average with a certain probability.

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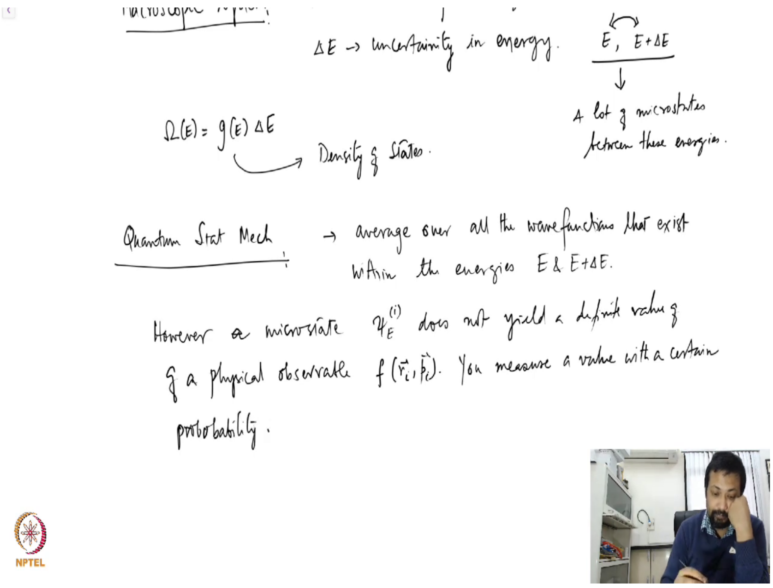

$\Delta E \to$ uncertainity in energy.

$E, E+\Delta E$

$\downarrow$

A lot of microstates between these energies.

$\Omega(E) = g(E)\,\Delta E$

$\to$ Density of States.

Quantum Stat Mech $\to$ average over all the wavefunctions that exist within the energies E & $E+\Delta E$.

However a microstate $\Psi_E^{(i)}$ does not yield a definite value of a physical observable $f(\vec{r}_i, \vec{p}_i)$. You measure a value with a certain probability.

So, you get a value with a certain so, you measure a value with a certain probability.

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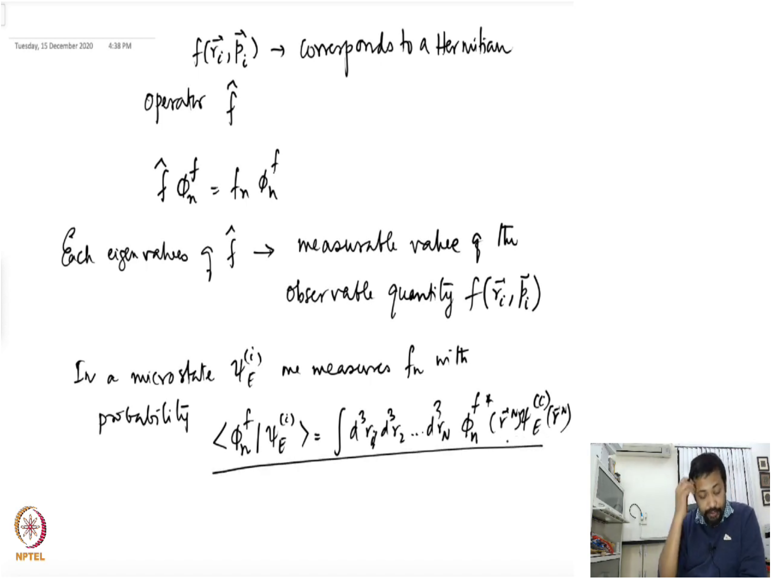

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$f(\vec{r}_i, \vec{p}_i) \rightarrow$ corresponds to a Hermitian operator $\hat{f}$

$$\hat{f}\,\phi_n^f = f_n\,\phi_n^f$$

Each eigenvalues of $\hat{f}$ $\rightarrow$ measurable value of the observable quantity $f(\vec{r}_i, \vec{p}_i)$

In a microstate $\psi_E^{(i)}$ one measures f_n with probability $\underline{\langle \phi_n^f | \psi_E^{(i)} \rangle = \int d^3r_1\, d^3r_2 \ldots d^3r_N\, \phi_n^{f*}(\vec{r}^N)\psi_E^{(i)}(\vec{r}^N)}$

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To be more explicit about this we consider this phase space observable f of r i, p i and this corresponds to a Hermitian operator f hat. Why Hermitian? Because it is a physical observable and therefore, you realize that the operator must be Hermitian. So, with a eigenvalues are real.

It has so since it is a Hermitian operator therefore, one can write down it is eigenvalue equation has f n phi f of n. Now, each eigenvalue of f n corresponds to a possible measurement of f, right. So, each eigenvalue of f hat this corresponds to a measurable value of the observable quantity f of r i comma p i.

Now, in a measurable state, sorry in a microstate psi E of i let us say the measure for damn it. Therefore, in a microstate psi i E one measures f n with the probability phi n psi i which is integral d cube r 1 d cube r 2 so on phi n f star r N psi i E star r N. One can see this just by expanding the wave function in the basis.

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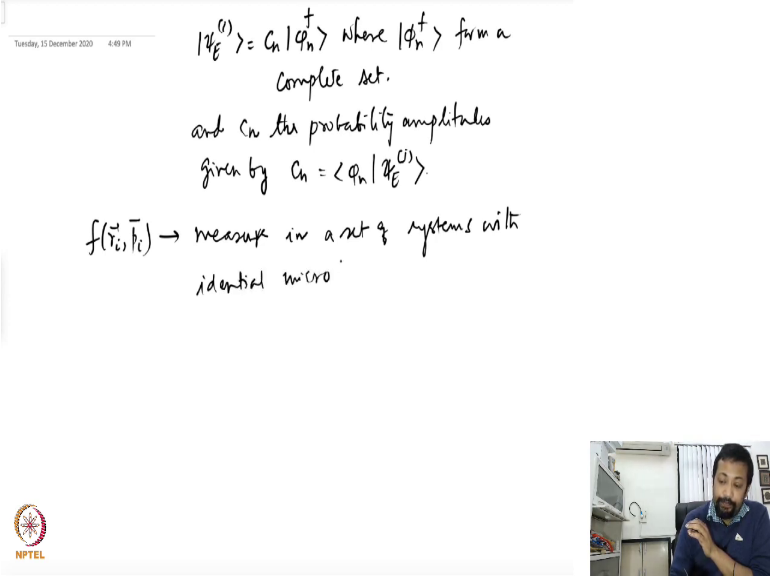

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$|\psi_E^{(i)}\rangle = C_n|\phi_n^{+}\rangle$ where $|\phi_n^{+}\rangle$ form a complete set.

and C_n the probability amplitudes given by $C_n = \langle\phi_n|\psi_E^{(i)}\rangle$.

$f(\vec{r}_i, \vec{p}_i) \rightarrow$ measure in a set of systems with identical micro

Psi E of i is equal to C n phi n where this one phi n the eigen functions form a complete set and C n are the probability amplitudes. They are the probability amplitudes given by phi n psi E i right. Now, if one performs measurement of the observable f of r i p i; so, if I performs the measurement of this observable let us say in a set of identical systems with the same microstate psi i. So, measure this in a set of systems with identical microstate.

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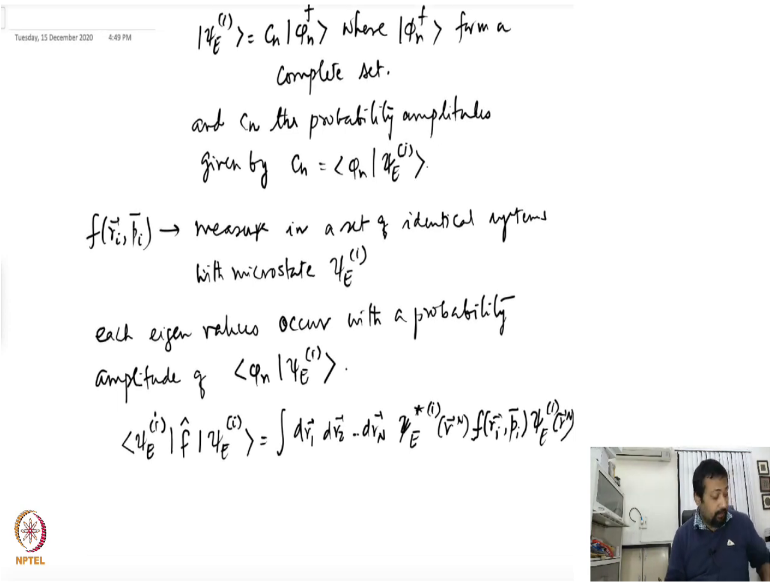

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$|\psi_E^{(i)}\rangle = c_n|\varphi_n^{f}\rangle$ where $|\phi_n^{f}\rangle$ form a complete set.

and c_n the probability amplitudes given by $c_n = \langle\varphi_n|\psi_E^{(i)}\rangle$.

$f(\vec{r}_i, \bar{p}_i) \rightarrow$ measure in a set of identical systems with microstate $\psi_E^{(i)}$

each eigen values occur with a probability amplitude of $\langle\varphi_n|\psi_E^{(i)}\rangle$.

$$\langle\psi_E^{(i)}|\hat{f}|\psi_E^{(i)}\rangle = \int d\vec{r}_1\, d\vec{r}_2 \ldots d\vec{r}_N\, \psi_E^{*(i)}(\vec{r}^N) f(\vec{r}_i, \bar{p}_i) \psi_E^{(i)}(\vec{r}^N)$$

So, you will see identical systems with the microstate in a set of identical systems with microstate in the same microstate psi E of i then each of the eigenvalues occur with the probability amplitude each of the eigenvalues with the probability amplitude of phi n psi E i. In quantum statistics so, one can write down this psi E i f is dr 1, dr 2, dr N psi E star i r N f r i p i psi E i r N, right.

Now, in quantum statistics another average adds to this one is no longer able to tell which specific microstate psi E i the system assures.

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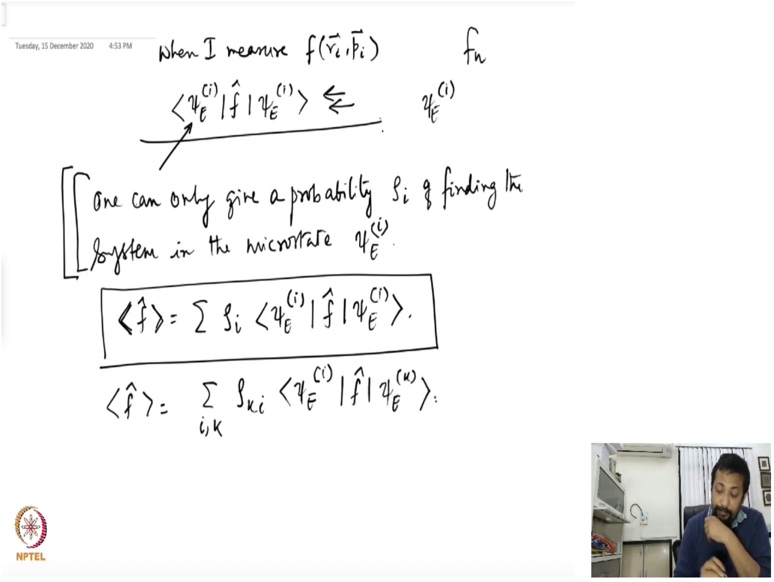
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When I measure $f(\vec{r}_i, \vec{p}_i)$ fn

$$\langle \psi_E^{(i)} | \hat{f} | \psi_E^{(i)} \rangle \leftleftarrows \qquad \psi_E^{(i)}$$

One can only give a probability ρ_i of finding the system in the microstate $\psi_E^{(i)}$.

$$\boxed{\langle \hat{f} \rangle = \sum \rho_i \langle \psi_E^{(i)} | \hat{f} | \psi_E^{(i)} \rangle.}$$

$$\langle \hat{f} \rangle = \sum_{i,k} \rho_{ki} \langle \psi_E^{(i)} | \hat{f} | \psi_E^{(k)} \rangle.$$

So, on top of it, so, when I measure this operator, this physical variable I get a value the eigenvalue with the average psi E i f hat psi E i but, on top of this you will have an in quantum statistic you will have another average that adds to it and why is that? Because you cannot see which microstate the system assures, right.

So, one can only give a probability. So, there is a one can only give a probability rho i with which well, the system will rho i of finding the system in the microstate, right. If now one performs a measurement of the observable in a set of such identical systems one can measure only the average of the quantum mechanical operator f cap or f hat weighted by this probability.

So, the average the expectation value of this is going to be sum over rho i psi E I right. This, however, is not the general expression. So, I hope it is now clear that may the difference that this average comes in right. So, if I start measuring a physical observable f in identical systems with the same microstate, then it is not I will get the eigenvalues f n we saw f n with a with a certain probability, right.

So, I measure this, but now the problem is you have prepared the system when you write down this you have prepared the system in a given microstate, but in reality when you measure it in a system this may not be. So, the system can be in any microstate, right and one cannot definitely say look the system is in this particular microstate psi E of i. It can be in a different microstate.

So, therefore, one can only give a probability of rho i you are finding the system in a given microstate and once you have this rho i this probability, then your actual expectation value of the average that you measure is a weighted average of this and this weight factor rho i is the probability of finding the system in the microstate psi E i, right. The most general expression of course, is given by f hat is sum over rho K, i psi E i f hat psi E of K.

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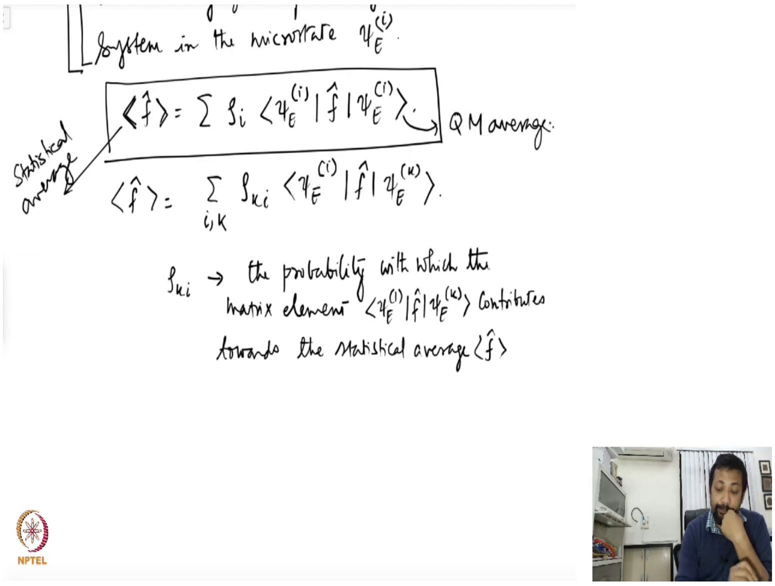

System in the microstate $\psi_E^{(i)}$.

$$\boxed{\langle \hat{f} \rangle = \sum \rho_i \langle \psi_E^{(i)} | \hat{f} | \psi_E^{(i)} \rangle.} \rightarrow \text{QM average.}$$

Statistical average

$$\langle \hat{f} \rangle = \sum_{i,k} \rho_{ki} \langle \psi_E^{(i)} | \hat{f} | \psi_E^{(k)} \rangle.$$

ρ_{ki} → the probability with which the matrix element $\langle \psi_E^{(i)} | \hat{f} | \psi_E^{(k)} \rangle$ contributes towards the statistical average $\langle \hat{f} \rangle$

The rho K i is now to be interpreted as a probability which the matrix element is the probability with which the matrix element contributes. So, the matrix element of this that we had written down psi E of i f hat psi E of k contributes towards the statistical average.

So, this quantity that you have written down over here is the statistical average and this is a quantum mechanical average that we are familiar with.

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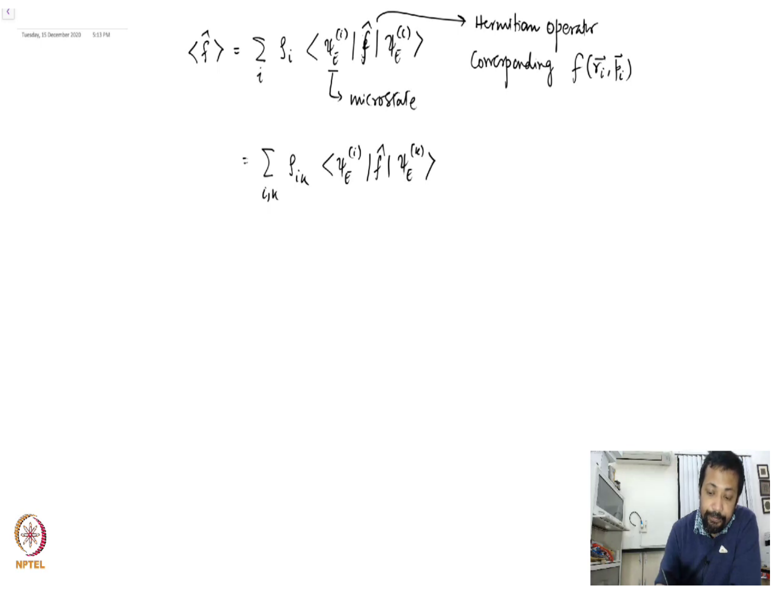

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$$\langle \hat{f} \rangle = \sum_i \rho_i \langle \underbrace{\psi_E^{(i)}}_{\rightarrow \text{ microstate}} | \hat{f} | \psi_E^{(i)} \rangle \rightarrow \text{Hermitian operator Corresponding } f(\vec{r}_i, \vec{p}_i)$$

$$= \sum_{i,k} \rho_{ik} \langle \psi_E^{(i)} | \hat{f} | \psi_E^{(k)} \rangle$$

So, we have the statistical average of an physical observable which was given by sum over i rho i psi E i f. This was the microstate in which we assume the system to be and this is the Hermitian operator corresponding to the microstate. Sorry, corresponding to the physical observable f r i p i and we said that the general expression this is not the general expression. The general expression can be written down as rho i, K psi E i f hat psi E of K.

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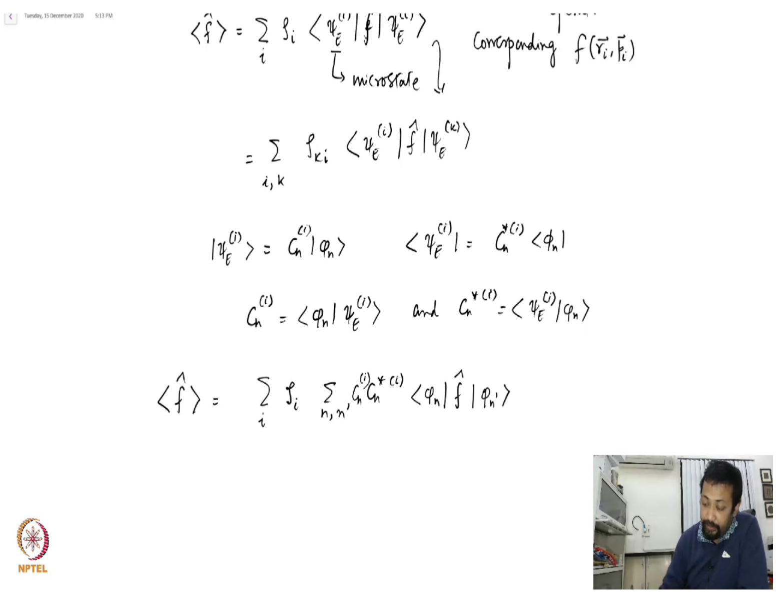

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$$\langle \hat{f} \rangle = \sum_i \rho_i \langle \psi_E^{(i)} | f | \psi_E^{(i)} \rangle$$

↳ microstate

Corresponding $f(\vec{r}_i, \vec{p}_i)$

$$= \sum_{i,k} \rho_{ki} \langle \psi_E^{(i)} | \hat{f} | \psi_E^{(k)} \rangle$$

$$|\psi_E^{(i)}\rangle = C_n^{(i)} |\varphi_n\rangle \qquad \langle \psi_E^{(i)}| = C_n^{*(i)} \langle \varphi_n|$$

$$C_n^{(i)} = \langle \varphi_n | \psi_E^{(i)} \rangle \quad \text{and} \quad C_n^{*(i)} = \langle \psi_E^{(i)} | \varphi_n \rangle$$

$$\langle \hat{f} \rangle = \sum_i \rho_i \sum_{n,n'} C_n^{(i)} C_n^{*(i)} \langle \varphi_n | \hat{f} | \varphi_{n'} \rangle$$

And, this is the my general expression the general expression is i comma K rho of K i psi E i f hat psi E of K to see how we can go from this to this one can expand the microstate as C n phi n, right and therefore, one has C n i star phi n, where C n i is equal to phi n psi E i and C n star i is equal to psi E i phi of n.

So, if we use this now and expand then we come up with f hat as sum over i rho of i sum over n comma n prime we will have C n star of i phi n f hat phi n prime and the C n of i, right.

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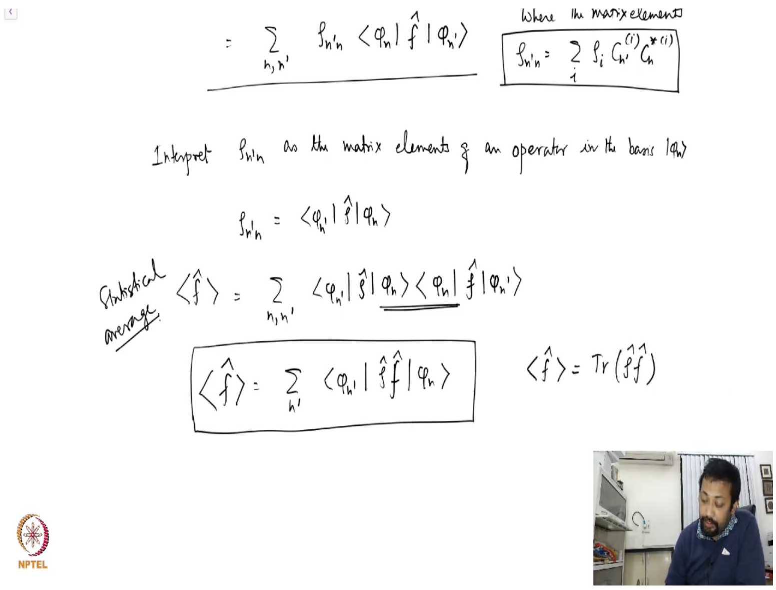

$$= \sum_{n,n'} \rho_{n'n} \langle \varphi_n | \hat{f} | \varphi_{n'} \rangle$$

Where the matrix elements

$$\boxed{\rho_{n'n} = \sum_i \rho_i C_{n'}^{(i)} C_n^{*(i)}}$$

Interpret $\rho_{n'n}$ as the matrix elements of an operator in the basis $|\varphi_n\rangle$

$$\rho_{n'n} = \langle \varphi_{n'} | \hat{\rho} | \varphi_n \rangle$$

Statistical average.

$$\langle \hat{f} \rangle = \sum_{n,n'} \langle \varphi_{n'} | \hat{\rho} | \underline{\underline{\varphi_n \rangle \langle \varphi_n |}} \hat{f} | \varphi_{n'} \rangle$$

$$\boxed{\langle \hat{f} \rangle = \sum_{n'} \langle \varphi_{n'} | \hat{\rho} \hat{f} | \varphi_n \rangle}$$

$$\langle \hat{f} \rangle = \mathrm{Tr}(\hat{\rho} \hat{f})$$

Sum over n comma n prime rho of n prime n phi n f hat phi n prime, where the matrix elements rho n prime n is given by sum over i rho i C n i C n star of i, right. Sorry, this has to be please be careful when this C n prime C n i star. Now, if I look at this particular expression now I can interpret rho n prime n as the matrix elements of an operator in the basis phi ns.

So that we can write rho n prime n is equal to phi n prime rho hat phi of n in which case this average this statistical average this is please note that this is the statistical average that we have said earlier also. This quantity then becomes sum over n n prime phi n prime rho hat phi n phi n f phi n prime. One can use one sum over the n and use the completeness of the basis to come up with the result n prime phi n prime rho hat f hat phi of n the statistical average of this physical observable becomes this, right.

In other words, this quantity is trace of rho hat f hat and it is to be noted that the trace is independent of the choice of the basis.

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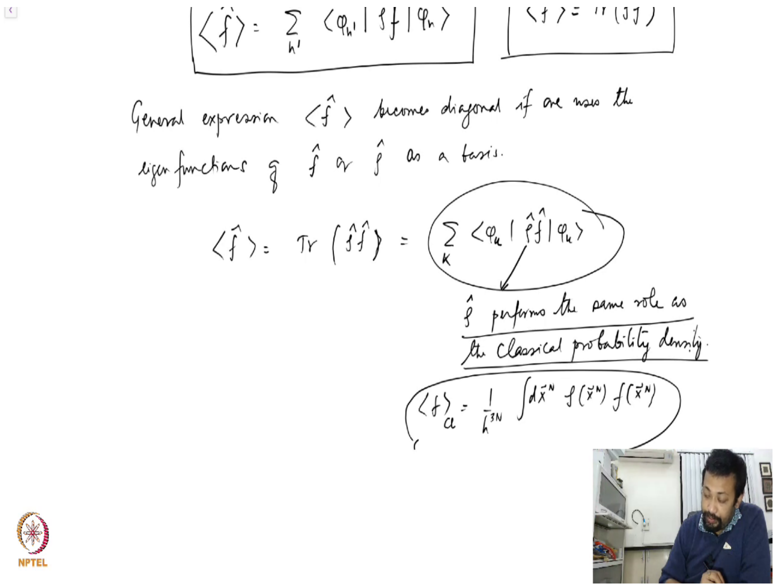

$\langle \hat{f} \rangle = \sum_{n'} \langle \varphi_{n'} | \rho f | \varphi_n \rangle$

$\langle f \rangle = \mathrm{Tr}(\rho f)$

General expression $\langle \hat{f} \rangle$ becomes diagonal if one uses the eigen functions of $\hat{f}$ or $\hat{\rho}$ as a basis.

$\langle \hat{f} \rangle = \mathrm{Tr}(\hat{\rho}\hat{f}) = \sum_{K} \langle \varphi_K | \hat{\rho}\hat{f} | \varphi_K \rangle$

$\hat{\rho}$ performs the same role as the classical probability density.

$\langle f \rangle_{cl} = \frac{1}{h^{3N}} \int d\vec{x}^N \rho(\vec{x}^N) f(\vec{x}^N)$

Further, the average the general expression the general expression for this quantity f hat becomes diagonal if one uses the eigen functions of f hat or rho hat as a basis. It is important to realize. So, therefore, what we have over here is essentially trace of rho hat f hat which is sum over K phi K rho cap f cap phi K, right.

It is important to realize therefore, that this quantity rho hat performs the same role as the classical probability density right, where we had the classical average f classical was 1 over h to the power n d of X N rho of X N times f of X N.

So, this was my classical average and this is my statistical average and I mean you can write it down in terms of integrals over coordinates that is also ok, then you will see that this performs the same role as the classical probability density.

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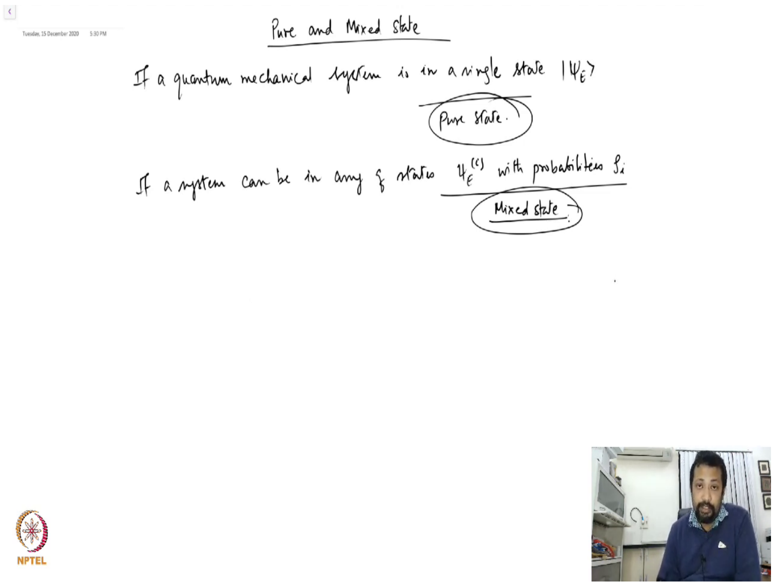

Pure and Mixed State

If a quantum mechanical system is in a single state $|\psi_E\rangle$

Pure state.

If a system can be in any of states $\psi_E^{(i)}$ with probabilities ρ_i

Mixed state

So, now we want to discuss pure and a mixed state. So, if a quantum mechanical system is in a given is in a single state psi of E, right. Then this is called a pure state. In contrast, if a system can be in any of the states psi of E i with probabilities rho i, then this is called a mixed state.

Now, given the system is either in a pure state or in a mixed state all the quantum mechanical and statistical averages can be calculated can be determined for any observable provided we know the form of the density matrix, right.

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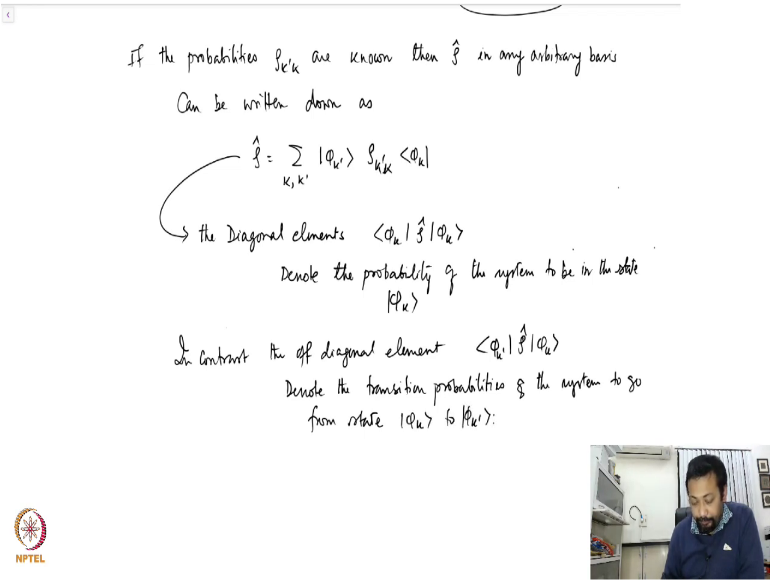

If the probabilities $\rho_{k'k}$ are known then $\hat{\rho}$ in any arbitrary basis Can be written down as

$$\hat{\rho} = \sum_{k,k'} |\phi_{k'}\rangle \rho_{k'k} \langle\phi_k|$$

the Diagonal elements $\langle\phi_k|\hat{\rho}|\phi_k\rangle$ Denote the probability of the system to be in the state $|\phi_k\rangle$

In contrast the off diagonal element $\langle\phi_{k'}|\hat{\rho}|\phi_k\rangle$ Denote the transition probabilities of the system to go from state $|\phi_k\rangle$ to $|\phi_{k'}\rangle$:

If the probabilities rho K prime K are known, then rho hat the density matrix in any arbitrary basis can be written down as rho hat is equal to sum over K comma K prime phi K prime rho K prime K phi of K, right. Now, here the diagonal elements which is phi of K rho hat phi of K, they denote the probabilities for the system of the system to be in the state phi of K.

In contrast the off diagonal elements which are essentially phi K prime rho hat phi of K they denote the transition probability of the system to go from state phi of K to phi of K prime.

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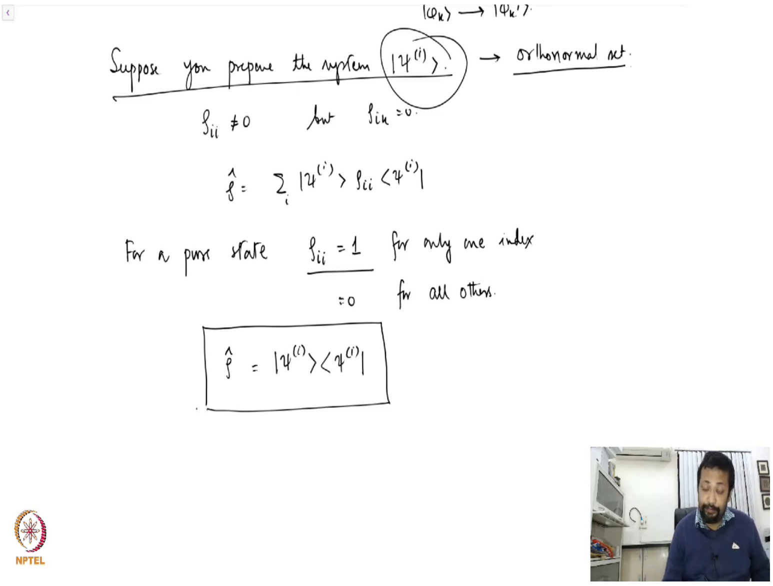

$|\phi_k\rangle \to |\psi_k'\rangle$

Suppose you prepare the system $|\psi^{(i)}\rangle$ → orthonormal set.

$\rho_{ii} \neq 0$ but $\rho_{ik} = 0$

$$\hat{\rho} = \sum_i |\psi^{(i)}\rangle \rho_{ii} \langle\psi^{(i)}|$$

For a pure state $\rho_{ii} = 1$ for only one index

$= 0$ for all others.

$$\boxed{\hat{\rho} = |\psi^{(i)}\rangle\langle\psi^{(i)}|}$$

You prepare this system psi i right and the set psi I they form an orthonormal set such that if you prepare the system in psi i such that your rho ii is nonzero, the diagonal elements are nonzero, but rho i K is equal to 0 which means there is no transition between the states which are allowed then your rho hat is sum over i psi i rho ii psi i right.

So, this sets they are an orthonormal set right which can always be done if you start off not with an orthonormal set you can always orthonormalize them by using the Gram Schmidt orthonormalization procedure, right. Please note that these do not form a complete set they do not span the whole of the Hilbert space.

But, be a subspace of the Hilbert space in which this state vector is precisely the state vector is not precisely determinable. For a pure state; for a pure state rho ii is equal to 1 for only one index and is equal to 0 for all others.

In this case, your density matrix takes the form psi E, sorry we will now simply the sum is now removed because rho ii is 0 for all others and for only a given value of i you have this rho ii is equal to 1 which means a probability of finding the system in that particular state is equal to 1 you are certain to find that there and all the other probabilities are 0. Therefore, for a pure state your density matrix take this particular form.

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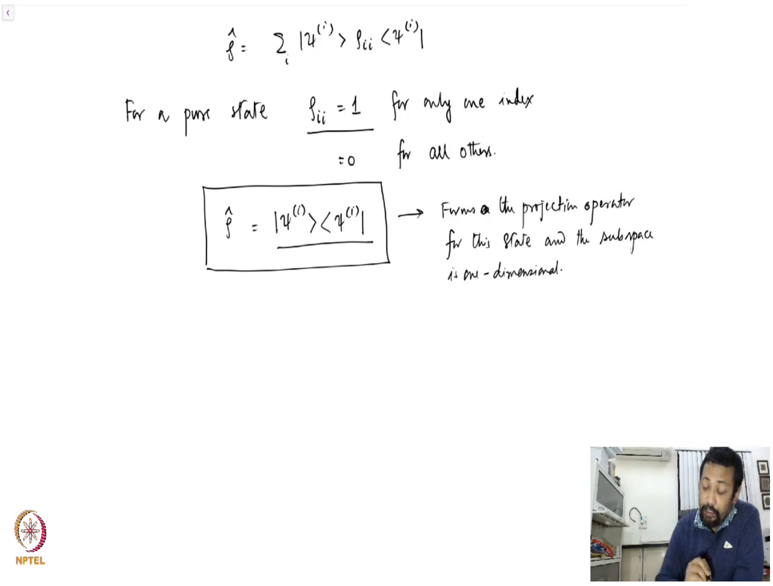

$$\hat{\rho} = \sum_i |\psi^{(i)}\rangle \rho_{ii} \langle \psi^{(i)}|$$

For a pure state $\underline{\rho_{ii} = 1}$ for only one index

$= 0$ for all others.

$$\boxed{\hat{\rho} = \underline{|\psi^{(i)}\rangle\langle\psi^{(i)}|}} \rightarrow$$

Forms the projection operator for this state and the subspace is one-dimensional.

Now, this quantity essentially forms a projection. So, projection operator for this state. So, rho hat is the projection operator for the state and the respective and the subspace is one-dimensional.