A. Introduction:
- In this lecture we derive the quantum mechanical fluctuation-dissipation theorem. We will first define the quantum Liouville operator, the density operator, and the essential features of quantum mechanical linear response theory...which leads to Kubo’s theorem and the quantum mechanical fluctuation dissipation theorem.
- Classical/Quantum Correspondences.
  - The classical distribution function \( f(X,t) \) corresponds to the quantum density matrix \( \rho(t) \). The equilibrium density operator is defined as
    \[
    \rho_{eq} = \frac{e^{-\beta H_0}}{Q} \quad \text{where} \quad Q = \sum_n e^{-iE_n t}
    \] (22.1)
  - We can get the equation of motion in the following way...
    \[
    \rho(t) = e^{iH_0 t} \rho_0 e^{-iH_0 t} \quad \text{then} \quad \frac{d\rho}{dt} = -\frac{i}{\hbar} [H, \rho] = -L \rho
    \] (22.2)
- The expectation value of a dynamical variable in quantum mechanics is
  \[
  \langle A(t) \rangle = Tr \left( A(t) \rho(t) \right) \quad \text{and} \quad \langle A(t) \rangle_{eq} = Tr \left( A(t) \rho_{eq} \right)
  \] (22.3)
- Therefore there is the correspondence between the classical ensemble average and the quantum mechanical average
  \[
  \langle A(t) \rangle_{\text{classical}} = \int dX A(X,t)f(X,t) \leftrightarrow \langle A(t) \rangle_{\text{quantum}} = Tr \left( A(t) \rho(t) \right)
  \] (22.4)

B. Density Operator: Pure State
- In the pure case the wave function for a system is known. Suppose the system is in a well-defined state but not an eigenstate of the Hamiltonian. The wave function corresponding to the jth state can be expanded in an orthogonal basis:
  \[
  \psi_j(t) = \sum_k C_{jk}(t) \varphi_k
  \] (22.5)
- The orthogonal basis set may be the eigenbasis of the Hamiltonian but this is not a necessity.
- The constants are defined as \( C_{jk}(t) = \int \psi_j^*(t) \varphi_k d\tau \)
- The expectation value of an observable in the jth state is
\[ \langle A(t) \rangle_j = \int \psi_j^* A \psi_j \, d\tau = \int \left[ \sum_k C_{jk} \varphi_k \right] A \left[ \sum_l C_{jl} \varphi_l \right] \, d\tau \]

\[ = \sum_{k,l} C^*_{jl} C_{kj} \int \varphi_k^* A \varphi_l \, d\tau = \sum_{k,l} \rho^*_{kl} A_{kl} = \text{Tr} \left( \rho^j (t) A \right) \]  

(22.6)

where \( \rho^j_{kl} = C^*_{jk} C_{jl} \) and \( \int \varphi_k^* A \varphi_l \, d\tau = A_{kl} \).

- The pure state density operator is Hermitian. The density operator has the following additional properties:
  - Conservation of probability: \( \text{Tr} \left( \rho^j (t) \right) = 1 \) and \( \frac{d}{dt} \text{Tr} \left( \rho^j (t) \right) = 0 \)
  - \( \dot{\rho}^j (t) = \frac{d\rho^j}{dt} = -\frac{i}{\hbar} [H, \rho^j (t)] \)
  - \( \langle A(t) \rangle_j = \text{Tr} \left( \rho^j (t) A \right) \)

- For the pure state case the density operator is mainly a matter of computational convenience. If wave function notation is used to express the properties given above generally more complicated expressions result:
  - \( \frac{d}{dt} \left| \psi^j (x) \right|^2 = 0 \)
  - \( i\hbar \frac{\partial \psi}{\partial t} = H\psi \)
  - \( \langle A(t) \rangle_j = \int \psi_j^* A \psi_j \, d\tau \)

- The first and third equations for the wave function are bilinear whereas the density operator equations are linear. Property two is a partial differential equation (i.e. Schrodinger’s equation) for a wave function, but is simply a commutator for the density operator.

C. Density Operator: Mixed State
- Suppose there exist uncertainty in the preparation of the state of a system. For example, we may consider an ensemble of systems that experience such complicated interactions that the wave function of a particular system cannot be known with complete certainty. Then the density matrix is

\[ \rho (t) = \sum_j P_j \rho^j (t) = \sum_j P_j \rho^j (t) \]  

(22.7)

where \( P_j \) is the probability of finding the system in the jth state.

- We now calculate the expectation value of an observable:
(22.8)

where \( \rho_{kl} = \sum_j P_j C_{jk}^* C_{jl} \)

### D. Mixed State Density Operator: Dirac Notation

- The mixed state density matrix can be conveniently expressed using Dirac notation:

\[
\rho(t) = \sum_j P_j |\psi_j\rangle \langle \psi_j| \tag{22.9}
\]

- Express the expansion of the wave function in the same orthogonal basis set in Dirac notation:

\[
|\psi_j\rangle = \sum_k C_{jk} \phi_k = \sum_k C_{jk} |k\rangle \tag{22.10}
\]

- Substitute (22.10) into (22.9):

\[
\rho(t) = \sum_j P_j |\psi_j\rangle \langle \psi_j| = \sum_j P_j \sum_{kl} C_{jk}^* C_{jl} |k\rangle \langle l|
\]

\[
= \sum_{kl} \sum_j P_j C_{jk}^* C_{jl} |k\rangle \langle l| = \sum_{kl} \rho_{kl} |k\rangle \langle l| \tag{22.11}
\]

- The expectation values of an observable \( A \) is now

\[
\langle A \rangle = \sum_j P_j \langle \psi_j | A | \psi_j \rangle = \sum_k \sum_j P_j \langle \psi_j | k \rangle \langle k | A | \psi_j \rangle
\]

\[
= \sum_k \sum_j P_j \langle k | A | \psi_j \rangle \langle \psi_j | k \rangle = \sum_k \langle k | \rho A | k \rangle = Tr(\rho A) \tag{22.12}
\]

- The equation of motion of the density operator is also conveniently obtained in Dirac notation:

\[
\frac{d\rho}{dt} = \frac{d}{dt} \sum_j P_j |\psi_j\rangle \langle \psi_j| = \sum_j P_j \left[ \left( \frac{d}{dt} |\psi_j\rangle \right) \langle \psi_j| + |\psi_j\rangle \left( \frac{d}{dt} \langle \psi_j| \right) \right]
\]

\[
= -\frac{i}{\hbar} \sum_j P_j \left[ (H |\psi_j\rangle) \langle \psi_j| - |\psi_j\rangle \langle \psi_j| H \right] = -\frac{i}{\hbar} [H, \rho] \tag{22.13}
\]