

Time-Dependent Statistical Mechanics

12. Quantum correlation functions

© Hans C. Andersen

November 4, 2009

1 Introduction

If A and B are classical variables and we are dealing with classical mechanics for a system, it is fairly clear what

$$A(t)B(t')$$

means for the physical system. It is a number that is a product of two numbers, each of which means the value of a property at a specific time, which can be calculated from the location of the system in phase space at that time. Then it is fairly clear what

$$\langle A(t)B(t') \rangle$$

means.

The quantum analog of this is far from obvious from this way of discussing it. Suppose $t > t'$. If we measure B at time t' , we perturb the state in an unpredictable way. This makes it less clear that a subsequent measurement of A at time t is a quantity that should appear in a physical theory.

We need the quantum analog of $A(t)B(t')$ and then of its ensemble average. To define these quantities, we will use the Heisenberg picture of quantum mechanics. Note that in the present discussion, we are merely laying the foundations by defining a general set of correlation functions. We will later

Continuation
of Lec-
ture 11
10/27/09

do a theoretical analysis of various experiments and show that these correlation functions are those that arise in a quantitative discussion of those experiments.

slide

Quantum correlation functions

In classical mechanics we have:

- dynamical variables, e.g. $A(\Gamma)$, $B(\Gamma)$
- time dependent dynamical variables, e.g. $A(t, \Gamma)$
- equilibrium ensemble averages, e.g. $\langle A \rangle$, $\langle A(t)B(0) \rangle$
- nonequilibrium ensemble averages

What are the quantum mechanical concepts that are most closely related to these classical concepts?

We will define those concepts using the Heisenberg representation of quantum mechanics.

Then we shall show how these quantities are related to experiments.

end of slide

2 Various formulations of quantum mechanics

General structure of quantum mechanics

In all versions of quantum mechanics,

- the state of the system is represented by a vector in a Hilbert space, e.g. $|\psi\rangle$,
- a dynamical variable is represented by an operator \hat{O}

Schrodinger picture

- states depend on time according to the Schrodinger equation

$$\frac{\partial}{\partial t}|\psi_S(t)\rangle = -\frac{i}{\hbar}\hat{H}_S(t)|\psi_S(t)\rangle$$

where

- $|\psi_S(t)\rangle$ is the Schrodinger state vector.
- $\hat{H}_S(t)$ = Hamiltonian operator in the Schrodinger picture. (The only time dependence is explicit, as in the time dependence of an external field.)
- operators are independent of time (except for any explicit time dependence because of aspects of the system that are under external control). The typical operator might be denoted \hat{O}_S .
- the expectation value of any physical quantity at time t is calculated from its operator \hat{O}_S and the state $|\psi_S(t)\rangle$ as

$$\langle\psi_S(t)|\hat{O}_S|\psi_S(t)\rangle$$

The solution of the Schrodinger equation can be expressed in the following form.

$$|\psi_S(t)\rangle = \hat{U}(t, t')|\psi_S(t')\rangle \quad (1)$$

$U(t, t')$ is sometimes called the time evolution operator or propagator. It operates on the wave function appropriate for time t' and generates the wave function for time t .

We can get the equation of motion for \hat{U} by substituting this into the Schrodinger equation, which gives

$$\frac{\partial}{\partial t}\hat{U}(t, t')|\psi_S(t')\rangle = -\frac{i}{\hbar}\hat{H}_S(t)\hat{U}(t, t')|\psi_S(t')\rangle$$

We want this to be true for all initial states $\psi_S(t')$, so the following operator equation must hold.

$$\frac{\partial}{\partial t}\hat{U}(t, t') = -\frac{i}{\hbar}\hat{H}_S(t)\hat{U}(t, t')$$

Start of material not covered in lecture in 2009

Moreover, we must have that

$$\hat{U}(t', t') = \hat{I}$$

where \hat{I} is the identity operator.

In the special case that the H_S is independent of time, the time evolution operator takes on an especially simple form.

$$\hat{U}(t, t') = \exp(-iH_S(t - t')/\hbar)$$

as can easily be verified.¹

End of material not covered in lecture in 2009

Heisenberg picture

In the Heisenberg picture, the state vector is independent of time but the operators depend on time.

- The Heisenberg state vector $|\psi_H\rangle$ (independent of time) is the $t = 0$ value of the Schrodinger state vector.

$$|\psi_H\rangle = |\psi_S(0)\rangle$$

- The Heisenberg operator \hat{O}_H is time dependent and is to be defined so that the expectation value of \hat{O} at time t is

$$\langle\psi_H|\hat{O}_H(t)|\psi_H\rangle$$

We demand that the expectation value calculated in this way should be consistent with what is obtained in the Schrodinger picture.

So we demand that

$$\langle\psi_H|\hat{O}_H(t)|\psi_H\rangle = \langle\psi_S(t)|\hat{O}_S|\psi_S(t)\rangle \quad (2)$$

¹Exponential operators can be defined in terms of their power series or in terms of their effects on energy eigenstates. In either case, if $\hat{H}_S|\phi\rangle = \epsilon|\phi\rangle$, then

$$\exp(-i\hat{H}_S t/\hbar)|\phi\rangle = e^{-i\epsilon t/\hbar}|\phi\rangle$$

It follows from Eq. (1) that

$$\begin{aligned} |\psi_S(t)\rangle &= \hat{U}(t, 0)|\psi_S(0)\rangle \\ \langle\psi_S(t)| &= \langle\psi_S(0)|\hat{U}^\dagger(t, 0) \end{aligned}$$

Thus the right side of Eq. (2) can be expressed as

$$\begin{aligned} \langle\psi_S(t)|\hat{O}_S|\psi_S(t)\rangle &= \langle\psi_S(0)|\hat{U}^\dagger(t, 0)\hat{O}_S U(t, 0)|\psi_S(0)\rangle \\ &= \langle\psi_S(0)|\hat{U}^\dagger(t, 0)\hat{O}_S U(t, 0)|\psi_S(0)\rangle \\ &= \langle\psi_H|\hat{U}^\dagger(t, 0)\hat{O}_S U(t, 0)|\psi_H\rangle \end{aligned}$$

Eq. (2) can be satisfied if we define the Heisenberg operators in the following way.

$$\hat{O}_H(t) \equiv \hat{U}^\dagger(t, 0)\hat{O}_S U(t, 0)$$

We adopt this definition.

In the special case that H_S is independent of time, this reduces to

$$\hat{O}_H(t) \equiv \exp(i\hat{H}_S t/\hbar)\hat{O}_S \exp(-i\hat{H}_S t/\hbar)$$

Incidentally, in this special case

$$\hat{H}_H(t) = \exp(i\hat{H}_S t/\hbar)\hat{H}_S \exp(-i\hat{H}_S t/\hbar) = H_S$$

(The exponential of \hat{H}_S commutes with \hat{H}_S itself, and this result follows.) Note that the result is independent of time. Thus it would be OK to write

$$\hat{O}_H(t) \equiv \exp(i\hat{H}t/\hbar)\hat{O}_S \exp(-i\hat{H}t/\hbar)$$

without specifying whether the \hat{H} in the exponent is H_S or $H_H(t)$, since the two are the same operator. Note that the simple exponential representation of U holds only in the case that H_S is independent of time.

3 Quantum ensembles and quantum ensemble averages

Earlier in the course, we defined precisely what we meant by classical ensemble averages. We now want to do the same thing for quantum ensemble

averages. Let's restrict our discussion to the canonical ensemble in which N and V are fixed. Classically, this has the effect of saying that all systems in the ensemble have the same Hamiltonian and can be represented as points in the same phase space. Quantum mechanically, this has the consequence that all systems in the ensemble have the same Hamiltonian and can be expanded in terms of the same eigenfunctions of the Hamiltonian.

In our discussion of classical ensemble averages, the basic elements of the discussion were:

1. The state of a system prepared according to a specific prescription is a random variable.
2. The state is specified by a point in phase space, Γ .
3. The quantity being averaged is a dynamical variable represented by a function of Γ , e.g. $A(\Gamma)$.
4. To calculate averages we need the probability distribution function of Γ . Call it $P(\Gamma)$.
5. The ensemble average of $A(\Gamma)$ is

$$\langle A \rangle = \int d\Gamma P(\Gamma) A(\Gamma)$$

6. For a preparation method that involves fixing the temperature of the system, the appropriate P is

$$P(\Gamma) = (\text{const.}) e^{-H(\Gamma)/k_B T}$$

These are the essential postulates of the classical canonical ensemble.

End of
Lecture
11
10/27/09

We now want to discuss the quantum mechanical analog of this.

Lecture
12
10/29/09

1. The state of a system prepared according to a specific prescription is a random variable. (This is the same as the classical statement.)
2. The state of the system is specified by a wave function. In general the wave function can be expanded in eigenstates of the Hamiltonian. Let ϕ_i satisfy

$$H\phi_i = E_i\phi_i$$

The wave function can then be expressed as

$$\psi = \sum_i c_i \phi_i$$

where the sum is over all of the eigenstates of the Hamiltonian. Thus the set of coefficients, c_i for all i , is what it takes to specify the wave function.

3. The quantity being averaged is a dynamical variable represented by a quantum mechanical operator \hat{A} . The quantum expectation value of A for a well defined quantum state ψ is

$$\langle \psi | \hat{A} | \psi \rangle$$

Note that this is a quantum mechanical expectation value, so it already is an average of some sort even for one system, but this is the quantity that must be averaged over all systems in the ensemble.

Using the basis function expansion for the wave function we get

$$\langle \psi | \hat{A} | \psi \rangle = \sum_{i,j} c_i^* c_j \langle \phi_i | \hat{A} | \phi_j \rangle$$

and this is to be averaged over all systems in the ensemble.

4. Note that all systems in the ensemble have the same basis functions and the same matrix elements. The only thing that varies from one system to another is the values of the coefficients c_i . To calculate the desired average, we need the ensemble average of $c_i^* c_j$.

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \sum_{i,j} \langle c_i^* c_j \rangle \langle \phi_i | \hat{A} | \phi_j \rangle$$

(By analogy with the classical case, you might have thought that we needed the distribution function of the set of coefficients $c_i, i = 1 \dots n$, but it is now clear that all we really need is averages of products of the form $\langle c_i^* c_j \rangle$.)

Let us define

$$\rho_{ji} = \langle c_j c_i^* \rangle = \langle c_i^* c_j \rangle$$

(Note the order of the factors and note which is complex conjugated.) This might or might not be the quantity you might initially want to define, but with this definition, we have the following compact result.

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \sum_{i,j} \rho_{ji} A_{ij}$$

The set of quantities ρ_{ij} represent a matrix that is called the ‘density matrix’. The set of matrix elements A_{ij} are also a matrix, and the sum on the right is the trace of the matrix product of the ρ and A matrices.² Thus we can write

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \text{Tr } \rho A$$

But any matrix can also be regarded as an operator (i.e. the operator whose matrix elements are the elements of the matrix). Thus, the density matrix can be regarded as the matrix of a density operator $\hat{\rho}$. So we also can write

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \text{Tr}(\hat{\rho} \hat{A})$$

where the quantity in parentheses is an operator product of two operators and hence is an operator. Here we are using the convention that

²The trace of a matrix is the sum of its diagonal elements. Thus, the trace of a matrix B is

$$\text{Tr} B = \sum_j B_{jj}$$

If the matrix B is the matrix product of two matrices C and D , then

$$B_{jk} = \sum_i C_{ji} D_{ik}$$

and

$$\text{Tr} B = \sum_{j,i} C_{ji} D_{ij}$$

the trace of an operator is the trace of the matrix of the operator, or the sum of the diagonal elements of the operator.

slide

Let us define

$$\rho_{ji} = \langle c_j c_i^* \rangle = \langle c_i^* c_j \rangle$$

Then

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \sum_{i,j} \rho_{ji} A_{ij}$$

The sum on the right is the trace of the matrix product of the ρ and A matrices. Thus

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \text{Tr } \rho A$$

But any matrix can also be regarded as an operator (i.e. the operator whose matrix elements are the elements of the matrix). Thus we also can write

$$\langle \langle \psi | \hat{A} | \psi \rangle \rangle = \text{Tr}(\hat{\rho} \hat{A})$$

end of slide

5. For a preparation method that involves fixing the temperature of the system, the appropriate density matrix is (assumed to be)

$$\hat{\rho} = (\text{const}) \times \exp(-\beta \hat{H})$$

In other words,

$$\begin{aligned} \rho_{ii} &= (\text{const}) \times \exp(-E_i/k_B T) \\ \rho_{ij} &= 0 \quad \text{for } i \neq j \end{aligned}$$

The ii diagonal element of ρ has meaning as the ensemble average of the probability that the system is in state i , and this probability is assumed to be proportional to the Boltzmann factor for the energy of state i . The assumption that the off-diagonal elements are zero would require some discussion to justify. We will not discuss this here. This assumption for the form of the density matrix in equilibrium quantum systems with specific N , V , and T is a basic postulate of equilibrium quantum statistical mechanics.

Thus, if we have any quantum mechanical operator \hat{O} , we define the *ensemble average of the operator \hat{O}* as

$$\langle \hat{O} \rangle = \text{Tr} \hat{\rho} \hat{O} = \sum_{ij} \rho_{ij} O_{ji}$$

If the ensemble is an equilibrium canonical ensemble, then

$$\hat{\rho} = (\text{const}) \times \exp(-\hat{H}/k_B T)$$

4 Definition of a quantum mechanical correlation function

Proposed definition of a quantum mechanical correlation function

For a system at equilibrium we define an average of the form

$$\langle \hat{A}_H(t) \hat{B}_H(t') \rangle$$

to be a quantum time correlation function of A and B .

You might think that this is a reasonable candidate for the definition of a quantum equilibrium correlation function. In fact it is reasonable, and functions of this type have some but not all of the properties of classical equilibrium correlation functions.

Stationarity property. Such correlation functions depend only on the time interval $t - t'$, not the individual time arguments. Let's show this.

$$\begin{aligned} \langle \hat{A}_H(t) \hat{B}_H(t') \rangle &= \text{Tr} [\hat{\rho} \hat{A}_H(t) \hat{B}_H(t')] \\ &= (\text{const}) \text{Tr} [\exp(-\beta \hat{H}) \exp(i\hat{H}t) \hat{A}_S \exp(-i\hat{H}t) \exp(i\hat{H}t') \hat{B}_S \exp(-i\hat{H}t')] \end{aligned}$$

Some elementary properties of operators

1. For any pair of operators \hat{C} and \hat{D} ,

$$Tr(\hat{C}\hat{D}) = Tr(\hat{D}\hat{C})$$

This is true even if the operators do not commute.

2. For any pair of operators \hat{C} and \hat{D} that *commute*,

$$\exp \hat{C} \exp \hat{D} = \exp \hat{D} \exp \hat{C}$$

3. For any operator \hat{C} and any two numbers a and b

$$\exp(a\hat{C}) \exp(b\hat{C}) = \exp((a + b)\hat{C})$$

Back to the calculation above.

Move the exponential on the far right to the far left. This does not change the value, because of the first property.

Commute it with the $\exp(-\beta\hat{H})$. This does not change the value because of the second property.

We get

$$\begin{aligned} \langle \hat{A}_H(t) \hat{B}_H(t') \rangle &= (const) Tr(\exp(-\beta\hat{H}) \exp(-i\hat{H}t') \exp(i\hat{H}t) \hat{A}_S \exp(-i\hat{H}t) \exp(i\hat{H}t') \hat{B}_S) \\ &= (const) Tr(\exp(-\beta\hat{H}) \exp(i\hat{H}(t - t')) \hat{A}_S \exp(-i\hat{H}(t - t')) \hat{B}_S) \end{aligned}$$

Thus we have shown that the equilibrium correlation function depends on the time interval not the absolute times. This is analogous to the behavior of classical time correlation functions.

Thus, we can define

$$S_{AB}(t - t') \equiv \langle \hat{A}_H(t) \hat{B}_H(t') \rangle$$

But this function lacks one important feature that the classical correlation function has.

Another elementary property of operators.

4. $\hat{A}_H(t)$ and $\hat{B}_H(t')$ do not in general commute. (The only common situation in which they commute is if \hat{A}_S commutes with \hat{B}_S and $t = t'$.)

Since these operators do not in general commute, it is *not* in general true that

$$S_{AB}(t - t') = S_{BA}(t' - t)$$

Accordingly, we define a symmetrized version of S by

$$\phi_{AB}(t) \equiv \frac{1}{2} (S_{AB}(t) + S_{BA}(-t))$$

It follows that

$$\phi_{AB}(t) = \phi_{BA}(-t)$$

which is analogous to the property of classical $C_{AB}(t)$.

We choose these definitions for several reasons.

- In quantum mechanical theories of absorption spectroscopy, scattering experiments, and relaxation processes, it is found that the measured quantities are often related to correlation functions defined in this way. They play the same role as the classical correlation functions do in classical theories of the same processes.
- In the limit that quantum effects are negligible, the behavior of $\phi_{AB}(t)$ and $S_{AB}(t)$ are similar to that of the classical correlation function $C_{AB}(t)$.
- The function $\phi_{AB}(t)$ has one of the symmetry properties of the classical $C_{AB}(t)$.

Note that there is another quantum correlation function that is often called $C_{AB}(t)$. We may or may not introduce it later.

5 General expression for a quantum correlation function

We can obtain a useful general expression for an equilibrium time correlation function in the canonical ensemble in the following way.

We use the fact that the Hamiltonian has no explicit time dependence.

We use a complete set of eigenfunctions $|i\rangle$ of \hat{H} .

$$\hat{H}|i\rangle = E_i|i\rangle$$

The set is complete. We assume the states are normalized.

The identity operator can be expressed as

$$\hat{I} = \sum_i |i\rangle\langle i|$$

Let \hat{A}_S and \hat{B}_S be Hermitian operators. Their matrix elements in this basis are

$$A_{ij} = \langle i|\hat{A}_S|i\rangle$$

and similarly for B_{ij} .

Then the S correlation function is

$$\begin{aligned} S_{AB}(t-t') &= \sum_i \rho_{ii} \langle i|\hat{A}_H(t)\hat{B}_H(t')|i\rangle \\ &= \sum_i \rho_{ii} \langle i|e^{i\hat{H}t/\hbar}\hat{A}_S e^{-i\hat{H}t/\hbar} e^{i\hat{H}t'/\hbar}\hat{B}_S e^{-i\hat{H}t'/\hbar}|i\rangle \\ &= \sum_i \rho_{ii} e^{iE_i(t-t')/\hbar} \langle i|\hat{A}_S e^{-i\hat{H}t/\hbar} e^{i\hat{H}t'/\hbar}\hat{B}_S|i\rangle \\ &= \sum_i \rho_{ii} e^{iE_i(t-t')/\hbar} \langle i|\hat{A}_S e^{-i\hat{H}(t-t')/\hbar}\hat{B}_S|i\rangle \\ &= \sum_{ij} \rho_{ii} e^{iE_i(t-t')/\hbar} \langle i|\hat{A}_S \sum_j |j\rangle\langle j| e^{-i\hat{H}(t-t')/\hbar}\hat{B}_S|i\rangle \\ &= \sum_{ij} \rho_{ii} e^{iE_i(t-t')/\hbar} \langle i|\hat{A}_S|j\rangle\langle j|e^{-iE_j(t-t')/\hbar}\hat{B}_S|i\rangle \\ &= \sum_{ij} \rho_{ii} e^{-i(E_j-E_i)(t-t')/\hbar} \langle i|\hat{A}_S|j\rangle\langle j|\hat{B}_S|i\rangle \\ &= \sum_{ij} \rho_{ii} e^{-i(E_j-E_i)(t-t')/\hbar} A_{ij} B_{ji} \end{aligned}$$

It is clear that the result is a function of the time interval rather than the two separate time arguments.

If we specialize to $A = B$, we have

$$\begin{aligned} S_{AA}(t) &= \sum_{ij} \rho_{ii} e^{-i(E_j - E_i)(t - t')/\hbar} A_{ij} A_{ji} \\ &= \sum_{ij} \rho_{ii} e^{-i(E_j - E_i)(t - t')/\hbar} A_{ij} A_{ij}^* \\ &= \sum_{ij} \rho_{ii} e^{-i(E_j - E_i)(t - t')/\hbar} |A_{ij}|^2 \end{aligned}$$

- Every correlation function is a sum of complex exponentials
 - with positive definite weights that come from the Boltzmann distribution of state energies
 - with amplitudes that depend on the matrix elements of the two operators.
- The frequency $(E_j - E_i)/\hbar$ appears if:
 - state i is occupied at the temperature of interest, and
 - the matrix element A_{ij} is nonzero, and
 - the matrix element B_{ji} is nonzero.
- For $t = 0$

$$S_{AB}(0) = \sum_{ij} \rho_{ii} A_{ij} B_{ji} = \langle \hat{A}_S \hat{B}_S \rangle$$

$$S_{AA}(0) = \sum_{ij} \rho_{ii} |A_{ij}|^2$$

The latter is positive definite.

slide

$$\begin{aligned}S_{AB}(t - t') &= \sum_{ij} \rho_{ii} e^{-i(E_j - E_i)(t - t')/\hbar} A_{ij} B_{ji} \\S_{AA}(t) &= \sum_{ij} \rho_{ii} e^{-i(E_j - E_i)(t - t')/\hbar} |A_{ij}|^2\end{aligned}$$

end of slide

We will ultimately need the Fourier transform of the correlation function, so we may as well calculate it now.

$$\begin{aligned}\hat{S}_{AB}(\omega) &= 2\pi \sum_{ij} \rho_{ii} \delta(\omega - (E_j - E_i)/\hbar) A_{ij} B_{ji} \\ \hat{S}_{AA}(\omega) &= 2\pi \sum_{ij} \rho_{ii} \delta(\omega - (E_j - E_i)/\hbar) |A_{ij}|^2\end{aligned}$$

Note that the latter is nonnegative for all frequencies, just like in the classical case.

We have not yet related this correlation function to absorption spectrum, but it will turn out that the $\hat{S}_{AA}(\omega)$ is closely related to absorption spectra, and it should look familiar. The absorption spectrum is a set of sharp lines at the usual frequencies with intensities that depend on the equilibrium populations of the various states and the matrix elements of various operators.

Lecture
12 con-
tinued
in N13