IP326. Lecture 16. Tuesday, Feb. 26, 2019

● Projection operator methods in the derivation of equations of motion and time correlation functions

In earlier lectures, we showed how, within the framework of linear response theory or continuum mechanics, the equations of motion of various dynamical variables could be used to derive expressions for transport coefficients in terms of time correlation functions. We'll now show how these same equations of motion can be transformed to an equivalent *exact* representation that lends itself more readily to systematic, well-controlled and physically motivated approximation schemes.

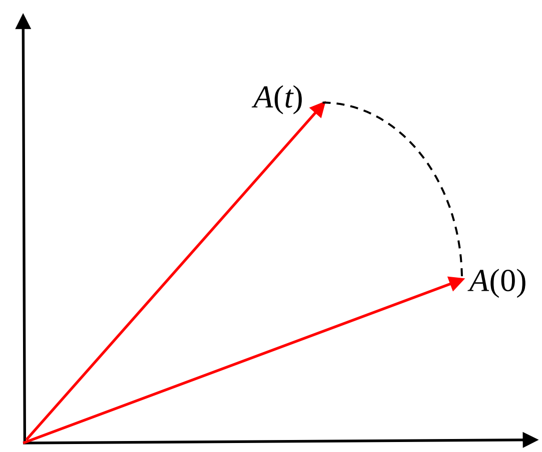
Recall that the time evolution of any dynamical variable A is dictated by the equation

$$\frac{dA(t)}{dt} = iLA(t) \qquad (1)$$

But being exact, this equation is analytically intractable for all but the simplest systems. Formally, however, its solution can be obtained at once:

$$A(t) = e^{itL}A(0) \qquad (2)$$

As we noted before, the operator e^{itL} is unitary, meaning, it preserves the norm of $A(0)$, merely changing its "orientation" over the course of the time interval t, but leaving its magnitude unaffected, as illustrated schematically in the figure below:



This allows us to think of $A(0)$ and $A(t)$ as vectors in phase space, and to employ the bra and ket notation of quantum mechanics to refer to them. We can reinforce this vector interpretation of a dynamical variable by noting that the time correlation function $C(t)$, defined as $C(t) = \int d\Gamma f_0(\Gamma) A^*(\Gamma) e^{itL} A(\Gamma)$, can be rewritten as

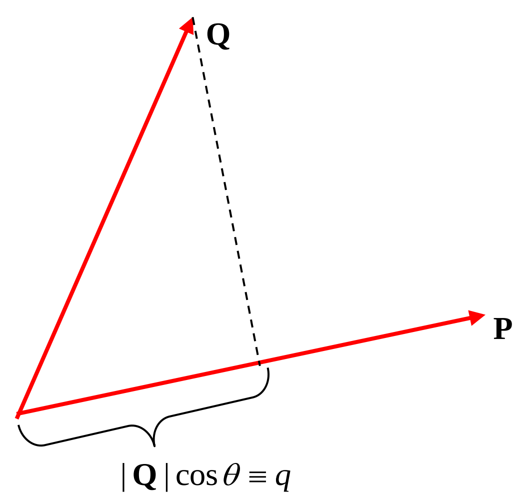
$$C(t) = \int d\Gamma (f_0^{1/2} A(\Gamma))^* e^{itL} f_0^{1/2} A(\Gamma) \tag{3a}$$

by virtue of the fact that f_0 is real and that $iLf_0 = 0$, making it possible to move $f_0^{1/2}$ to the left of the operator e^{itL} without affecting anything. In (3a), the combination $f_0^{1/2} A$ can be regarded in an abstract sense as a "wavefunction" ψ_A. In other words, $\psi_A(\Gamma) \equiv f_0^{1/2}(\Gamma) A(\Gamma)$. The important thing to note about this function is that for any property A that has a finite ensemble average, ψ_A will be square integrable, meaning, $\int d\Gamma |\psi_A(\Gamma)|^2 < \infty$; so ψ_A is effectively a vector in the Hilbert space of functions of Γ (cf. Berne and Pecora.) In any case, we have the relation

$$C(t) = \int d\Gamma \psi_A^*(\Gamma) \psi_A(\Gamma, t) \equiv \langle A | A(t) \rangle \tag{3b}$$

where $|A\rangle = \psi_A(\Gamma)$, $|A\rangle^* = \langle A| = \psi_A^*(\Gamma)$, and $|A(t)\rangle = \psi_A(\Gamma(t)) = \psi_A(\Gamma, t)$. It will always be understood that when a bra and ket are multiplied together, integration over Γ is implied.

Equation (3b) is entirely analogous to the scalar product in quantum mechanics, with $|A\rangle$ representing a "state vector". The product of two such vectors can therefore be interpreted in a way analogous to the way we interpret the dot product in algebra, which for any two vectors **P** and **Q** is denoted $\mathbf{P} \cdot \mathbf{Q}$, and is defined as $|\mathbf{P}||\mathbf{Q}|\cos\theta$, where θ is the angle between the vectors. Here, $|\mathbf{Q}|\cos\theta \equiv q$ is the magnitude of the projection of **Q** onto **P**, and is illustrated in the figure below



The projection q can also be written as $q = |\mathbf{Q}| \left(|\mathbf{P}||\mathbf{Q}| \right)^{-1} \mathbf{P} \cdot \mathbf{Q}$.

The time correlation function $\langle A | A(t) \rangle$ may be viewed similarly, as a scalar product in phase space, in which the initial state of the system, represented by $| A(0) \rangle$, is multiplied by the projection of the time-evolved state, $| A(t) \rangle$, onto it. In analogy with the dot product, we can therefore say that

$$\text{Projection of } | A(t) \rangle \text{ onto } | A(0) \rangle = | A \rangle \langle A | A \rangle^{-1} \langle A | A(t) \rangle \tag{4}$$

This interpretation of the term projection is meaningful in that by using (4) to calculate the projection of $| A(0) \rangle$ onto $| A(0) \rangle$, we get

$$| A \rangle \langle A | A \rangle^{-1} \langle A | A(0) \rangle = | A \rangle \langle A | A \rangle^{-1} \langle A | A \rangle$$

$$= | A \rangle$$

which is what we *should* get. So given these facts, we can formally define the operation of projecting any vector (i.e., any dynamical variable) onto $| A \rangle$ through the introduction of a projection operator *P*, defined as

$$P = | A \rangle \langle A | A \rangle^{-1} \langle A | \tag{5}$$

and such that

$$P | A(t) \rangle = | A \rangle \langle A | A \rangle^{-1} \langle A | A(t) \rangle \tag{6}$$

The scalar product of $P | A(t) \rangle$ with $| A \rangle$ is therefore given by

$$\langle A | P | A(t) \rangle = \langle A | A \rangle \langle A | A \rangle^{-1} \langle A | A(t) \rangle$$

$$= \langle A | A(t) \rangle$$

This means that a time correlation function can be thought of as a measure of the amount of a dynamical variable at time *t* that is correlated with, or that has a component lying along, the same or different dynamical variable at time 0.

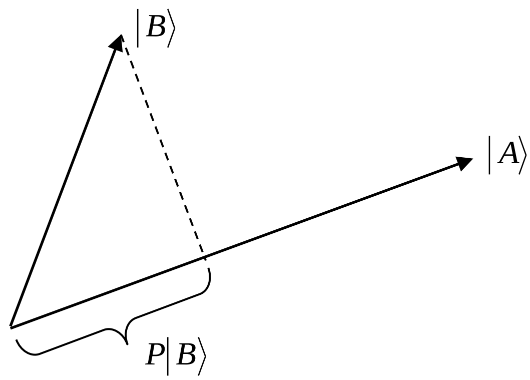
● Properties of the projector P

1. Idempotency

Consider the action of P on the "state vector" $\psi_B(\Gamma) = |B\rangle$. By definition

$$P|B\rangle = |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

which is some other state vector. Geometrically, it corresponds to the line segment shown in the figure below



Now imagine acting P on $P|B\rangle$; the result is

$$\begin{aligned} PP|B\rangle \equiv P^2|B\rangle & \\ &= |A\rangle\langle A|A\rangle^{-1}\langle A|A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle \\ &= |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle \\ &= P|B\rangle \qquad (7) \end{aligned}$$

In other words, $P^2 = P$, which makes P an idempotent operator.

2. Hermiticity

Consider the scalar product of the vector $|A\rangle$ and the vector $P|B\rangle$. By definition this product is

$$\langle A|P|B\rangle = \langle A|A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

$$= \langle A|B\rangle \tag{8}$$

Now consider the scalar product of the vector $|B\rangle$ with the vector $P|A\rangle$, which is

$$\langle B|P|A\rangle = \langle B|A\rangle \tag{9}$$

But recall that $\langle B|A\rangle^* = \langle A|B\rangle$, which means that

$$\langle B|P|A\rangle^* = \langle A|B\rangle$$

and so

$$\langle A|P|B\rangle = \langle B|P|A\rangle^*$$

$$= \langle B|PA\rangle^*$$

$$= \langle PA|B\rangle$$

Thus, $\langle A|PB\rangle = \langle PA|B\rangle$, which makes P a Hermitian operator.

● The orthogonal projector Q

It will prove useful in the developments to follow to introduce an operator Q defined as $Q \equiv 1 - P$. According to this definition,

$$Q = 1 - |A\rangle\langle A|A\rangle^{-1}\langle A| \tag{10}$$

and so, as one immediate consequence,

$$Q|A\rangle = |A\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|A\rangle$$

$$= 0 \tag{11}$$

which means that the action of Q is to project out of $|A\rangle$ a part that has no component lying along it. We'll see, therefore, that the action of Q is effectively to project a dynamical variable onto the "space" orthogonal to $|A\rangle$.

Other properties of Q

1. Like P, the operator Q is also idempotent, as demonstrated below by its action on a vector $|B\rangle$:

$$Q|B\rangle = |B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

Therefore,

$$QQ|B\rangle = Q^2|B\rangle$$

$$= Q|B\rangle - Q|A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

$$= |B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle + |A\rangle\langle A|A\rangle^{-1}\langle A|A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

$$= |B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle + |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

$$= |B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

$$= Q|B\rangle$$

Thus, $Q^2 = Q$.

2. Q is also Hermitian. The proof is as follows: Consider the action of Q on $|B\rangle$.

$$Q|B\rangle = |QB\rangle = |B\rangle - |A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

Therefore,

$$\langle C|QB\rangle = \langle C|B\rangle - \langle C|A\rangle\langle A|A\rangle^{-1}\langle A|B\rangle$$

$$= \langle C|B\rangle - \langle A|B\rangle\langle A|A\rangle^{-1}\langle C|A\rangle$$

It follows that

$$\langle C|QB\rangle^* = \langle B|C\rangle - \langle B|A\rangle\langle A|A\rangle^{-1}\langle A|C\rangle$$

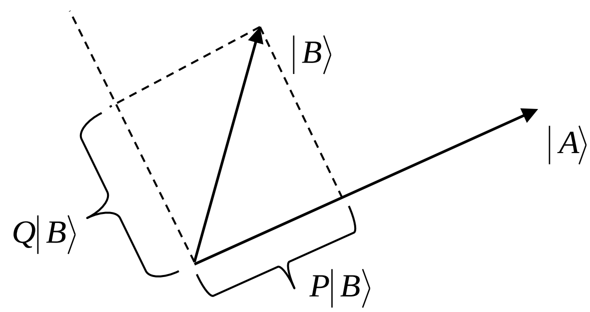
$$= \langle B|(1 - |A\rangle\langle A|A\rangle^{-1}\langle A|)|C\rangle$$

$$= \langle B|QC\rangle$$

Hence, $\langle C|QB\rangle = \langle B|QC\rangle^* = \langle QC|B\rangle$, and so Q is Hermitian. The Hermiticity of Q also implies that

$$\langle A|QB\rangle = \langle QA|B\rangle = 0 \tag{12}$$

which means that $Q|B\rangle = |QB\rangle$ is "orthogonal" to $|A\rangle$. And what this means geometrically is illustrated below:



Together, these two operators, P and Q, provide a way of rewriting the Liouville equation for the evolution of the dynamical variable A in an alternate, highly convenient form. Before seeing how this is done, we'll first establish some general operator identities.

● <u>Identity 1</u>

If M and N are any two operators, then

$$(M+N)^{-1} = M^{-1} - M^{-1}N(M+N)^{-1} \tag{13}$$

<u>Proof</u>

Apply both sides of this equation to the operator $M + N$. On the LHS, this leads to the identity operator I, while on the RHS it leads to

$$M^{-1}(M+N) - M^{-1}NI = I + M^{-1}N - M^{-1}N = I$$

So the operators on both sides of (13) are equivalent.

• Identity 2

$$(I+M)^{-1}=\sum_{n=0}^{\infty}(-M)^n \tag{14}$$

Proof

Apply both sides of the equation to the operator $I+M$. On the LHS this yields I; on the RHS we have

$$\sum_{n=0}^{\infty}(-M)^n(I+M)=\sum_{n=0}^{\infty}(-M)^n-\sum_{n=0}^{\infty}(-M)^{n+1}$$

$$=I+\sum_{n=1}^{\infty}(-M)^n-\sum_{j=1}^{\infty}(-M)^j$$

$$=I$$

So the operators on both sides of (14) are equivalent.

• Identity 3

$$e^{-(M+N)t}=e^{-Mt}-\int_0^t dt' e^{-M(t-t')}Ne^{-(M+N)t'} \tag{15}$$

Proof

To prove this result, we first need to provide a meaning to the Laplace transform of an exponential operator. So consider $\int_0^{\infty} dte^{-st}e^{-Mt}$, which we shall understand as follows:

$$\int_0^{\infty} dte^{-st}e^{-Mt}=\int_0^{\infty} dte^{-st}\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}M^n t^n$$

$$=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}M^n\int_0^{\infty} dte^{-st}t^n$$

$$=\sum_{n=0}^{\infty}\frac{(-1)^n}{n!}M^n\frac{n!}{s^{n+1}}$$

$$= \frac{1}{s}\sum_{n=0}^{\infty}\left(-\frac{M}{s}\right)^{n} = \frac{1}{s}\left(I + \frac{M}{s}\right)^{-1} \qquad \text{(Identity 2)}$$

$$= \left(s + M\right)^{-1} \tag{16}$$

Now consider the operator $(s + M + N)^{-1}$ and rewrite it using Identity 1. This yields

$$(s + M + N)^{-1} = (s + M)^{-1} - (s + M)^{-1} N (s + M + N)^{-1} \tag{17}$$

Assuming that s is a Laplace variable, we next take the inverse Laplace transform (which we'll denote L^{-1}) of both sides of (17), producing

$$L^{-1}(s + M + N)^{-1} = L^{-1}(s + M)^{-1} - L^{-1}\tilde{f}(s)\tilde{g}(s) \tag{18}$$

where $\tilde{f}(s) \equiv (s + M)^{-1}$ and $\tilde{g}(s) \equiv N(s + M + N)^{-1}$.

Now, as we'll show right away, the Laplace inverse of a product of Laplace transformed functions is the convolution of the original functions. That is

$$L^{-1}\tilde{f}(s)\tilde{g}(s) = \int_0^t dt' f(t - t')g(t') \tag{19}$$

To prove (19), we take the Laplace transform of both sides of the equation. The LHS obviously just recovers $\tilde{f}(s)\tilde{g}(s)$ itself, and so

$$\tilde{f}(s)\tilde{g}(s) = \int_0^{\infty} dt e^{-st} \int_0^t dt' f(t - t')g(t')$$

$$= \int_0^{\infty} dt \int_0^{\infty} dt' e^{-st}\theta(t - t') f(t - t')g(t')$$

$$= \int_0^{\infty} dt' \int_0^{\infty} dt e^{-st}\theta(t - t') f(t - t')g(t')$$

$$= \int_0^{\infty} dt' \int_{t'}^{\infty} dt e^{-st} f(t - t')g(t') \tag{20}$$

Now rewrite the terms in argument of the exponential as $s(t - t' + t')$ and then introduce the change of variable $x \rightarrow t - t'$, which converts (20) to

$$\tilde{f}(s)\tilde{g}(s) = \int_0^\infty dt' \int_0^\infty dx e^{-sx} e^{-st'} f(x) g(t') = \tilde{f}(s)\tilde{g}(s)$$

thus establishing (19).

If we apply these results to (18), after recalling that $L^{-1}(s+a)^{-1} = e^{-at}$, we end up with

$$e^{-(M+N)t} = e^{-Mt} - \int_0^t dt' e^{-M(t-t')} N e^{-(M+N)t'}$$

thus, proving Identity 3.