IP326. Lecture 17. Thursday, Feb. 28, 2019

● An exact equation of motion for the time evolution of a dynamical variable

The projection operators P and Q introduced in the last lecture, and defined as $P = |A\rangle\langle A|A\rangle^{-1}\langle A|$ and $Q = 1 - |A\rangle\langle A|A\rangle^{-1}\langle A|$, will now be used to derive a new equation of motion for the dynamical variable $A(t)$. We've already established that the time evolution of $A(t)$ is determined by the equation

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

where L is the Liouvillian. The formal solution of Eq. (1) is $A(t) = e^{iLt}A(0)$, and if this solution is substituted back into Eq. (1), the result is

$$\frac{dA(t)}{dt} = iLe^{iLt}A(0) = e^{iLt}iLA$$

which in bra-ket notation becomes

$$\frac{d|A(t)\rangle}{dt} = e^{iLt}iL|A\rangle \tag{2}$$

The introduction of a factor of unity into Eq. (2) in the form $1 = P + Q$ leads to

$$\frac{d|A(t)\rangle}{dt} = e^{iLt}(P+Q)iL|A\rangle$$

$$= e^{iLt}PiL|A\rangle + e^{iLt}QiL|A\rangle \tag{3}$$

Consider the first term on the RHS of Eq. (3); using the definition of P in this term, we get

$$e^{iLt}PiL|A\rangle = e^{iLt}|A\rangle\langle A|A\rangle^{-1}\langle A|iLA\rangle$$

$$\equiv ie^{iLt}|A\rangle\Omega$$

$$= i\Omega|A(t)\rangle \tag{4}$$

where $\Omega \equiv \langle A|A\rangle^{-1}\langle A|LA\rangle$ is a quantity we shall refer to as a "frequency".

To treat the second term on the RHS of Eq. (3), we first recall the operator identity $e^{-(M+N)t} = e^{-Mt} - \int_0^t dt' e^{-M(t-t')} N e^{-(M+N)t'}$, which can be rearranged to

$$e^{-Mt} = e^{-(M+N)t} + \int_0^t dt' e^{-M(t-t')} N e^{-(M+N)t'} \tag{5}$$

If we now set the operators M and N in this relation to be $-iL$ and PiL, respectively, we arrive at the identity

$$e^{iLt} = e^{QiLt} + \int_0^t dt' e^{iL(t-t')} PiL e^{QiLt'} \tag{6}$$

which we then use with the expression $e^{iLt} QiL|A\rangle$ from Eq. (3) to produce

$$e^{iLt} QiL|A\rangle = e^{QiLt} QiL|A\rangle + \int_0^t dt' e^{iL(t-t')} PiL e^{QiLt'} QiL|A\rangle \tag{7}$$

The structure of Eq. (7) suggests that it may be helpful to introduce a new state vector $|F(t)\rangle$, defined as

$$|F(t)\rangle = e^{QiLt} QiL|A\rangle \tag{8}$$

This function has some interesting properties. Consider what happens when we take its scalar product with the vector $|A\rangle$; the result is

$$\langle A|F(t)\rangle = \langle A|e^{QiLt} QiL|A\rangle \tag{9}$$

After expanding out the exponential, this becomes

$$\langle A|F(t)\rangle = \langle A|\left(1 + QiLt + \frac{1}{2!} QiLtQiLt + \cdots\right) QiL|A\rangle$$

$$= \langle A|QiLA\rangle + t\langle A|QiLQiL\rangle + \frac{t^2}{2!}\langle A|QiLQiLQiL\rangle + \cdots \tag{10}$$

In all of the terms in Eq. (10), the leftmost Q can be moved into the bra because of hermiticity, so all these terms will contain the factor $\langle QA| = (|QA\rangle)^*$, which is 0, and so $\langle A|F(t)\rangle = 0$. In other words, $|F(t)\rangle$ is orthogonal to the initial value of A, viz., $|A\rangle$, at all times. This makes $|F(t)\rangle$ akin to a random variable, since at no time do such variables have any correlation at all with a dynamical variable. For this reason, we'll refer to $|F(t)\rangle$ as a generalized random force (although, strictly speaking, its time evolution is entirely deterministic.)

The action of Q on $|F(t)\rangle$ is also revealing; it is given by

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

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

$$= |F(t)\rangle$$

so $|F(t)\rangle$ lies in the space orthogonal to $|A\rangle$.

After substituting Eqs. (4), (7) and (8) into Eq. (3), the evolution equation for $|A(t)\rangle$ is transformed to

$$\frac{d|A(t)\rangle}{dt} = i\Omega|A(t)\rangle + \int_0^t dt' e^{iL(t-t')} PiL|F(t')\rangle + |F(t)\rangle \tag{11}$$

A few additional manipulations of Eq. (11) can be carried out, specifically on the function $PiL|F(t')\rangle$ in the second term, which is now treated as follows:

$$PiL|F(t')\rangle = PiLQ|F(t')\rangle \qquad \text{(because } Q|F(t)\rangle = |F(t)\rangle\text{)}$$

$$= (1-Q)iLQ|F(t')\rangle$$

$$= iLQ|F(t')\rangle - QiLQ|F(t')\rangle$$

$$= iLQ|F(t')\rangle - (1-|A\rangle\langle A|A\rangle^{-1}\langle A|)iLQ|F(t')\rangle$$

$$= |A\rangle\langle A|A\rangle^{-1}\langle A|iLQ|F(t')\rangle \tag{12}$$

Because both L and Q are Hermitian, Eq. (12) can be rewritten as

$$PiL|F(t')\rangle = i|A\rangle\langle A|A\rangle^{-1}\langle QLA|F(t')\rangle$$

$$= -|A\rangle\langle A|A\rangle^{-1}\langle QiLA|F(t')\rangle \tag{13}$$

Recalling the definition of the generalized force in Eq. (8), we see that the term $\langle QiLA|$ in Eq. (13) is just the value of this force at time 0, viz., $(|F\rangle)^*$. If we now put these results back in Eq. (11), we get

$$\frac{d|A(t)\rangle}{dt} = i\Omega|A(t)\rangle - \int_0^t dt' e^{iL(t-t')}|A\rangle\langle A|A\rangle^{-1}\langle F|F(t')\rangle + |F(t)\rangle \tag{14}$$

For convenience, we'll now introduce a function $K(t)$ defined as

$$K(t) \equiv \langle A|A\rangle^{-1}\langle F|F(t')\rangle \tag{15}$$

We'll refer to it as a "memory function" (for reasons that will become clear later.) At the same time, let's notice that $e^{iL(t-t')}|A\rangle$ is nothing but $|A(t-t')\rangle$, which means that Eq. (14) finally reduces to

$$\frac{d|A(t)\rangle}{dt} = i\Omega|A(t)\rangle - \int_0^t dt'|A(t-t')\rangle K(t') + |F(t)\rangle$$

or more conventionally to

$$\frac{d|A(t)\rangle}{dt} = i\Omega|A(t)\rangle - \int_0^t dt' K(t-t')|A(t')\rangle + |F(t)\rangle \tag{16}$$

after the change of variable $x \to -t' + t$ in the integral on the right hand side.

Equation (16) is known as the generalized Langevin equation or GLE. It is exact, and is an alternative, equivalent form of the Liouville equation, but its structure makes it more amenable to the introduction of well-controlled physically motivated approximations, as we'll see.

By taking the scalar product of the terms on both sides of Eq. (16) with the initial state vector $|A\rangle$ (and recalling that $\langle A|F(t)\rangle = 0$), the equation can be converted to one for the time correlation function $C(t) = \langle A|A(t)\rangle$; specifically,

$$\frac{dC(t)}{dt} = i\Omega C(t) - \int_0^t dt' K(t-t')C(t), \tag{17}$$

which is sometimes referred to as the memory function equation.

● Generalization to many variables

The foregoing results apply to the case of just a single dynamical variable (such as the x component of the position or the z component of the momentum), but they are easily generalized to the case where the dynamical variable is actually a vector and has several components (such as the position and momentum of a set of, say, 5 particles in an ensemble of N particles in a space of 3 dimensions, which can be regarded as a vector with a total of 30 components.) For such cases, the dynamical variables will be represented by boldface symbols. So a variable denoted $\mathbf{A}$ (or $|\mathbf{A}\rangle$) stands for the vector $\mathbf{A} = (A_1, A_2, \ldots, A_n)$. The time autocorrelation function of $\mathbf{A}$ is now a matrix $\mathbf{C}(t) = \langle \mathbf{A} | \mathbf{A}(t) \rangle$ that is given by

$$\mathbf{C}(t) = \begin{pmatrix} \langle A_1 | A_1(t) \rangle & \cdots & \cdots & \langle A_1 | A_n(t) \rangle \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \langle A_n | A_1(t) \rangle & \cdots & \cdots & \langle A_n | A_n(t) \rangle \end{pmatrix} \tag{18}$$

The projector P likewise has the following more general definition

$$P = |\mathbf{A}\rangle \langle \mathbf{A} | \mathbf{A} \rangle^{-1} \langle \mathbf{A} | = \sum_{i,j} | A_i \rangle \langle A_i | A_j \rangle^{-1} \langle A_j | \tag{19}$$

and $Q = 1 - P$ is defined similarly. Given these definitions, it can be shown (and you should try showing it yourselves) that the same sequence of steps that led to the generalized Langevin equation for a single variable (Eq. (16)), leads, in the case of a vector variable, to

$$\frac{d|\mathbf{A}(t)\rangle}{dt} = i\mathbf{\Omega} \cdot |\mathbf{A}(t)\rangle - \int_0^t dt' \mathbf{K}(t - t') \cdot |\mathbf{A}(t')\rangle + |\mathbf{F}(t)\rangle \tag{20a}$$

and

$$\frac{d\mathbf{C}(t)}{dt} = i\mathbf{\Omega} \cdot \mathbf{C}(t) - \int_0^t dt' \mathbf{K}(t - t') \cdot \mathbf{C}(t) \tag{20b}$$

where $|\mathbf{F}(t)\rangle = e^{QiLt} QiL |\mathbf{A}\rangle$, with

$$\mathbf{\Omega}(t) = \begin{pmatrix} \langle A_1|A_1\rangle & \cdots & \cdots & \langle A_1|A_n\rangle \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \langle A_n|A_1\rangle & \cdots & \cdots & \langle A_n|A_n\rangle \end{pmatrix}^{-1} \begin{pmatrix} \langle A_1|LA_1\rangle & \cdots & \cdots & \langle A_1|LA_n\rangle \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \langle A_n|LA_1\rangle & \cdots & \cdots & \langle A_n|LA_n\rangle \end{pmatrix} \tag{21}$$

and

$$\mathbf{K}(t) = \begin{pmatrix} \langle A_1|A_1\rangle & \cdots & \cdots & \langle A_1|A_n\rangle \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \langle A_n|A_1\rangle & \cdots & \cdots & \langle A_n|A_n\rangle \end{pmatrix}^{-1} \begin{pmatrix} \langle F_1|F_1(t)\rangle & \cdots & \cdots & \langle F_1|F_n(t)\rangle \\ \vdots & \ddots & & \vdots \\ \vdots & & \ddots & \vdots \\ \langle F_n|F_1(t)\rangle & \cdots & \cdots & \langle F_n|F_n(t)\rangle \end{pmatrix} \tag{22}$$

The derivation of these results makes use of the orthogonality condition $\langle \mathbf{A}|\mathbf{F}(t)\rangle = \mathbf{0}$, which translates to the condition $\langle A_i|F_j(t)\rangle = 0, \forall i, j$.

In component form Eqs. (20a) and (20b) are given by

$$\frac{d|A_i(t)\rangle}{dt} = i\sum_j \Omega_{ij}|A_j(t)\rangle - \sum_j \int_0^t dt' K_{ij}(t-t')|A_j(t')\rangle + |F_i(t)\rangle \tag{23a}$$

$$\frac{dC_{ij}(t)}{dt} = i\sum_k \Omega_{ik} C_{kj}(t) - \sum_k \int_0^t dt' K_{ik}(t-t') C_{kj}(t) \tag{23b}$$

● Symmetry properties of the time correlation functions

1. We've shown earlier that if a dynamical variable A_i transforms under time reversal as $\gamma_i A_i$, where $\gamma_i = \pm 1$, then the correlation function $\langle A_i|A_j\rangle = 0$ if $\gamma_i \neq \gamma_j$. This means that if a vector variable $\mathbf{A}$ has some subset of components $\mathbf{A}_E$ that are even under time reversal, meaning $\mathbf{A}_E \to \mathbf{A}_E$, and another subset $\mathbf{A}_O$ that are odd under time reversal, meaning $\mathbf{A}_O \to -\mathbf{A}_O$, such that it's possible to write

$$\mathbf{A} = \begin{pmatrix} \mathbf{A}_E \\ \mathbf{A}_O \end{pmatrix} \tag{24}$$

then the equilibrium correlation function $\langle \mathbf{A}|\mathbf{A}\rangle$, by the symmetry property above, acquires a block symmetric matrix structure. That is,

$$\langle \mathbf{A} | \mathbf{A} \rangle = \begin{pmatrix} \langle \mathbf{A}_E | \mathbf{A}_E \rangle & \mathbf{0} \\ \mathbf{0} & \langle \mathbf{A}_O | \mathbf{A}_O \rangle \end{pmatrix} \tag{25}$$

This further means that

$$\langle \mathbf{A} | \mathbf{A} \rangle^{-1} = \begin{pmatrix} \langle \mathbf{A}_E | \mathbf{A}_E \rangle^{-1} & \mathbf{0} \\ \mathbf{0} & \langle \mathbf{A}_O | \mathbf{A}_O \rangle^{-1} \end{pmatrix} \tag{26}$$

A further implication is that the frequency matrix $\mathbf{\Omega}$ vanishes unless A_i and A_j have *different* signatures under time reversal.

Proof: By definition, $\Omega_{ij} = \sum_k \langle A_i | A_k \rangle^{-1} \langle A_k | LA_j \rangle$. Under time reversal $L \to -L$, while $A_i \to \gamma_i A_i$, so it follows that

$$\Omega_{ij} \to \gamma_i \gamma_k \gamma_k \gamma_j \sum_k \langle A_i | A_k \rangle^{-1} \langle A_k | LA_j \rangle = -\gamma_i \gamma_j \Omega_{ij}$$

And therefore γ_i and γ_j must have opposite signs for $\mathbf{\Omega}$ to be non-vanishing. Because of this property, $\mathbf{\Omega}$ also has a block diagonal structure, but of the form

$$\Omega = \begin{pmatrix} \mathbf{0} & \mathbf{\Omega}_{EO} \\ \mathbf{\Omega}_{EO} & \mathbf{0} \end{pmatrix} \tag{27}$$

where the off-diagonal matrices couple variables of different time reversal symmetry.

2. Another result proved earlier is that under time reversal, the time correlation function $C_{ij}(t) \equiv \langle A_i | A_j(t) \rangle$ transforms as

$$C_{ij}(t) \to \gamma_i \gamma_j C_{ij}(-t) = \gamma_i \gamma_j C^*{}_{ji}(t)$$

Thus if A_i and A_j have the same signature under time reversal, $C_{ij}(t)$ is an even function of time, while if they have different signatures, then $C_{ij}(t)$ is an odd function of time. As a further corollary, the time autocorrelation function $C_{ii}(t)$ is a real, even function of time.