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Comparison of Four Methods for Obtaining Time Autocorrelation Functions

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It is shown that the continued fraction representation of autocorrelation functions can be obtained by applying the operator-algebra method. The method is compared with Mori's memory function formalism, the moment expansion approach of Lado et al. based on the Schmidt orthogomalization process and the recurrence relation method developed by Lee.

I. INTRODUCTION

There has been considerable attention given to finding methods for direct evaluation of the time autocorrelation functions since the original work was initiated by Lowe and Norberg.[1] Time autocorrelation functions are an important physical quantity and constitute a branch of nonequilibrium ststistical mechanics. Actually they have been applied to many interesting physical problems concerning magnetic susceptibilities, electronic conductivities, NMR spectra and so on.[2-5]

Several general approaches have been devised so far. Zwanzig[6] developed projection operators to select out only the relevant information contained in the full dynamical expressions. Mori[7] derived the exact generalized Langevin equation for a dynamical variable using a projection operator technique and obtained an expression for the Laplace transform of a time autocorrelation function as a continued fraction representation.

On the other hand, several different types of approach have also been reported for the problem. Lado, Memory, and Parker[8] obtained the representation by expending the by dynamical variable in terms of an orthogonal set. More recently, Lee[9] got the representation by utilizing the recurrence relation method.

There is an alternative way to reach the generalized Langevin equation. It involves proceeding directly from the Laplace transform of the time autocorrelation function and taking the algebraic expansion of the inverse operator.[10] This technique will be referred to as the operator-algebra method.

In the present paper, first we shall precisely review the other theories with our main concerns on the calculation of the time autocorrelation function. Then we apply the operator-algebra methodto direct evaluation of the time autocorrelation function.

II. FOUR APPROACHES

1. Mori's theory

If, for a dynamical variable A in a many body system with Hamiltonian H,$[H,A]$ $HA-AH\neq 0$, then the time evolution in the Heisenberg picture is formally given by $A(t)=\exp(iHt)a\ \exp(-iHt)$,where $A=A(0)$ and $h=1$.

The information about $A(t)$ helps us obtain$\langle A(t)A(0)\rangle$, somtimes called the time autocorrelation function,where the bracket denotes the ensemble average.

The equation of motion is given by

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

where L is the Liouville operator corresponding to H.

The standard Mori theory is based on the assunmption that L is Hermitian, i,e.,

$$(LF, G^*)=(F, [LG]^*) \tag{2}$$

for arbitrary linear operators F and G, where G^* is the Hermition conjugate of G and (A, B) is any binary operation of two variables A and B.

For our purpose we construct a biorthogonal set of vectors and the correspon-ding projection operators. The quantity A, which generates succesive basis vectors $f_1, f_2, \quad f_n$, forms a Hilbert space. The projection of vector G onto the f_j axis is given by

$$P_j G \equiv (G, f_j^*)^{-1} f_j, \quad (j=0,1, \qquad n) \tag{3}$$

where $f_j = fL_j f_{j-1} \geq 1, L_j = (1-P_{j-1}) L_{j-1}, f_0 = A$ and $L_0 = L$. By a suitable extension of the standard Mori approach, we obtain for the time evolutoon of the dynamical variables $f_j(t)$

$$df_j(t)/dt = i\omega_j f_j(t) - \int_0^t \phi_j(t-s) f_j(s) ds + f_{j+1}(t) \tag{4}$$

or

$$f_j(t) = \Xi_j(t) f_j + \int_0^t \Xi_j(s) f_{j+1}(t-s) ds, \tag{5}$$

where

$$\Xi_j(t) = (f_j(t), f_j^*)/(f_j, f_j^*), \tag{6}$$
$$i\omega_j = (iL_j f_j, f_j^*)/(f_j, f_j^*), \tag{7}$$
$$\phi_j(t) = (f_{j+1}(t), f^*_{j+1})/(f_j, f_j^*). \tag{8}$$

If we take $j=0$, then Eq.(4) leads to a generalized Langevin equation. The variable $f_{j+1}(t)$ is regarded as a random force. Using the above equations and connsidering the orthogonality condition, we obtain the integro-differential equations for $\Xi_j(t)$ as

$$d\Xi_j(t)/dt = i\omega_j \Xi_j(t) - \int_0^t \phi_j(t-s) \Xi_j(s) ds. \tag{9}$$

It should be noted that Eq.(9) is given in terms of the memory function $\phi(t)$. By taking Laplace transform(LT) of Eq.(9), we have

$$\tilde{\Xi}_j(z) = [z - i\omega_j + \tilde{\Xi}_{j+1}(z) \Delta^2_{J+1}]^{-1} \tag{10}$$

where

$$\tilde{\Xi}(z) \equiv LT\Xi(t) = \int_0^{\infty} \Xi(t)\exp(-zt)dt, \quad (11)$$

$$\Delta^2_{J+1} \equiv (f_{j+1}, f^*_{j+1})/(f_j, f_j^*). \quad (12)$$

Applying Eq.(9) successively, we can get a continued fraction expansin of the hierarchy equations to higher order Ξfunction. So far we introduced the continued fraction representation for the Laplace transform of time autocorrelation functions on the basis of memory function formalism.

2. Moment Expansion Approach with Orthogonal Functions

Lado et al.[8] applied a schmidt orthogonalization process for calculation of the magnetic moment autocorrelation function $G(t)$ in the line shape of the *NMR* spectrum.

Let us consider the formal solution of the equation of motion for the magnetic moment fluctuation $A(t)$ with the Hermitian Liouvillian operator L in Hilbert space,[11]

$$|A(t)) = \exp(itL)|A(0)) = \sum_{J=0}^{\infty} \frac{(it)^j}{j!}|L^j A(0)). \quad (13)$$

This expansions leads directly to the moment expansion for $G(t)$. To compute the projection of $|A(t)$ onto the first, or $j=0$,the following are defined using the Schmidt orthogonalization process:

$$|o) = |A(0)), \quad (14a)$$

$$|j) = L^J|A(0)) - \sum_{K=0}^{J-1} \frac{(k|L^J|A(0))}{(k|k)}|k). \quad (14b)$$

Than $|A(t))$ may be represented in this basis set as

$$|A(t)) = \sum_{j=0}^{\infty} a_j(t)|j) \tag{15}$$

where $a_j(t) = (j|A(t)/(j|j)$, and in particular,
$a_0(t) = (A(0)|A(t))$ and $(A(0)|(A(0)) = G(t)/G(0)$
Futher, we can obtain the algebraic equationas for the coefficients $a_j(t)$.
These are formally solved using the Laplace transform representation to give

$$(iz + \omega_0)\tilde{a}_0(z) + \nu_0^2 \tilde{a}_1(z) = i, \tag{16a}$$

$$\tilde{a}_{j-1}(z) + (iz + \omega_j)\tilde{a}_j(z) + \nu_j^2 \tilde{a}_{j+1}(z) = 0 \tag{16b}$$

where $\nu_j^2 = (j+1\ |j+1)/(j|j)$, $\omega_j = (j|L|j)/(j|j)$ and $\tilde{a}_j = (z)LT[a_j(t)]$
Here ν_j^2, ω_j and $\tilde{a}_j$ correspond to Δ^2_{J+1}, $i\omega_j$ and $\tilde{\Xi}(z)$ delta with in the previous section. respectively.

We then have the solution

$$\tilde{G}(z)/G(0) = \tilde{a}_0(z) = iD_1(z)/D_0(z) \tag{17}$$

where $D_j(z)$is an infinite order determinant of the form

$$D_j(z) = \begin{vmatrix} iz+\omega_j & \nu_j^2 & 0 & \cdots \\ 1 & iz+\omega_{j+1} & \nu_{j+1}^2 & \cdots \\ 0 & 1 & iz+\omega_{j+2} & \ddots \\ \vdots & \vdots & \vdots & \end{vmatrix} \tag{18}$$

By expanding in minors of the first row, we easily obtain a recursion relation for the determinants $D_j(z)$:

$$D_j(z) = (iz + W_j)D_{j+1}(z) - \nu^2{}_j D_{j+2}(z). \tag{19}$$

Repeated use of Eq(19) in the denominator of Eq.(17) leads an infinite continued fraction of the hierarchical equation for $\tilde{a}_0(z)$:

$$\tilde{a}_0(z) = \cfrac{1}{z - i\nu_0 + \cfrac{\nu^2_0}{z - i\nu_1 + \cfrac{\nu^2_1}{z - i\nu_1 + \cdots}}} \qquad (20)$$

This equation is the same as Eq.(10) for j=o.

3. The Recurrence Relation Method Developed by Lee[9]

It was shown that variable A(t) may be given in terms of an orthogonal expansion as

$$A(t) = \sum_{j=o}^{\infty} a_j(t) f_j \qquad (21)$$

where $\{a_j(t)\}$ is a set of time dependent real functions and $\{f_j\}$ is a set of orthogonalized basis vectors spanning the space which is realized by the liner product. For simplicity, it is assumed that A is Hermitian.

It is well known that basis set$\{f_j\}$ satisfies the recurrence relation

$$f_{j+1} = \dot{f}_j + \bar{\Delta}_j f_{j-1}, \quad j \geq 0, \qquad (22)$$

where $\dot{f}_j = iLf_j$, $\bar{\Delta}_j = (f_j f_j)/(f_{j-1}, f_{j-1})$, $f_{-1}=0$ and $\bar{\Delta}_0=1$. It is to be noted that $\bar{\Delta}$,corresponds to $\bar{\Delta}^2_j$ of Mori or ν^2_{j-1} of Lado et al.

Further, Eq.(22) yields a recurrence relation for $\{a_j(t)\}$:

$$\bar{\Delta}_{j+1}\, a_{j+1}(t) = -\dot{a}_j(t) + a_{j-1}(t), \quad j \geq 0 \qquad (23)$$

where $\dot{a}_j(t) = da_j(t)/dt$ and $a_{-1}(t)=0$. By applying the Laplace transform (LT) on Eq.(23), we obtain

$$1 = z\tilde{a}_0(z) + \bar{\Delta}_1 \tilde{a}_1(z), \qquad (24a)$$

$$a_{j-1}(z)=za_j(z)+\Delta_{j+1}a_{j+1}(z),\ j\geq 1 \tag{24b}$$

where $a_j(z)=LT[a_j(t)]$.Eqs.(24a) and (24b) correspond to Eqs. (16a) and (16b) respectively. The main difference is that the factor w_j, which appears in the approaches of Mori and Lado et al. does not appear here. This results from the fact that all the f_j are Hermitian [see Eq.(35) or Ref.12]. Extension to the non-Hermitian case can be realized by starting from the first principle. Eqs. (24a) and (24b) may be combined to generate the following continued fraction,

$$\tilde{a}_0=(z)=z+\cfrac{1}{\cfrac{\Delta_1}{z+\cfrac{\Delta_2}{z+\cdots}}} \tag{25}$$

which agrees with Eq.(20) except for the ω term.

4. OPERATOR-algebra Method

Here we will show that the Laplace transform of time autocorrelation functions can be expressed as a continued fraction by applying the operator-algebra method.

From Eq.(6) we have

$$\begin{aligned}\tilde{\Xi}_j(z)&= LT[(f_j(t),f_j^*)/(f_j(t),f_j^*)]\\ &= ((z-iL)^{-1}f_j,f_j^*)/f_j,f_j^*)\end{aligned} \tag{26}$$

Which can be rewritten into the following form by using Mori's projection operator:

$$\begin{aligned}&\tilde{\Xi}_j(z)((z-iL_j\ P_j-iL_j\ P_j')^{-1}f_j,f_j^*)/(f_j,f_j^*)\\ &=(\{(z-iL_j\ P_j')^{-1}+(z-iL_j\ P_j')^{-1}iL_jP_j\\ &\quad(z-iL_j)^{-1}\}\ f_j,f_j^*)/(f_j,f_j^*)\end{aligned} \tag{27}$$

where $P_j'=1-P_j$ and $z-iL_j=z-iL_jP_j-iL_j\ P_j'$ have been used.

The first part of Eq.(27) can be calculated as

$$((z-iL_jP_j')^{-1} f_j, f_j^*)=(\{ \frac{1}{z} + \frac{1}{z} iL_jP_j'\frac{1}{z} + \cdots \} f_j, f_j^*)=(f_j, f_j^*)/z \qquad (28)$$

since $(L_j P_j' f_j, f_j^*)=0$. The second part can be calculated by using

$$P_j(z-iL_j)^{-1}f_j=((z-iL_j)^{-1} f_j, f_j^*)\cdot(f_j, f_j^*)^{-1}\cdot f_j = \tilde{\Xi}_j(z)\cdot f_j. \qquad (29)$$

Inserting Eqs.(28) and (29) into Eq.(27) we obtain

$$\tilde{\Xi}_j(z)=[z-(iL_jf_j, f_j^*)\cdot(f_j, f_j^*)^{-1} -(iL_jP_j'(z-iL_j P_j')^{-1} iL_jf_j, f_j^*)\cdot(f_j, f_j^*)^{-1}]^{-1}. \qquad (30)$$

In order to simplify the problem, we assume that L is Hermitian. We also consider the following relations:

$$P_j'(z-iL_j P_j')^{-1} = \sum_{n=o}^{oo} (P_j' iL_j \frac{1}{z})^n P_j' = (z-P_j' iL_j)^{-1} P_j' \qquad (31)$$

and

$$((z-iP'_jL_j)^{-1}P'_jiL_jf_j, (P_jiL_jf_j)^*) = 0. \qquad (32)$$

when then obtain

$$\Xi_j(z)= z-i\omega_j + \left[\frac{((z-iL_{j+1})^{-1}f_{j+1}, f^*_{j+1})}{(f_{j+1}, f^*_{j+1})} \cdot \frac{(f_{j+1}, f^*_{j+1})}{(f_j, f^*_j)} \right]^{-1} \qquad (33)$$

which can rewritten as

$$\Xi_j(z)=[z-i\omega_j + \Xi_{j+1}(z) \cdot \Delta^2_{j+1}]^{-1} \qquad (34)$$

where

$$\Xi_{j+1}(z)\equiv((z-iL_{j+1})^{-1}f_{j+1}, f^*_{j+1})/(f_{j+1}, f^*_{j+1}). \qquad (35)$$

Eq.(35)is similar in form to Eq.(26)and can be calculated further with the same procedure,leading to the continued fraction. This show $\Xi_j(z)$ could be directly expressed using the continued fraction representation without utilizing the memory function formalism as in

Eq.(9).

III. CONCLUDING REMARKS

It has been shown that the Laplace transform of time autocorrelation functions can be given as an infinte continued fraction by applying the operator-algebra method.

The theoories mentioned in the last section seem to have different theoretical backgrounds at first sight. However, these approaches lead to identical results. Under careful examination, we see that they involve orthogonalization processes such as the Gram-Schmidt process. Thus we can say that the method involing the projection operator technique is a formal interpretation, from a different standpoint, of the Gram-Schmidt process.

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[11] Here, the magnetic moment fluctuation m(t) in Ref. 8 has been replaced by A(t) for convenience and the inner product is defined as (A|B)=<A+B> for arbitrary operators A and B, where $A^+$is the Hermitian conjugate of A and the angular bracket denotes and equilibrium thermal average.

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