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A Note on the Asymptotic Master Equations for Systems with Bound States

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It is shown that, within the convolutionless formalism of Fuliński, the asymptotic form (in time) of the Liouville equation does not change with the existence of bound states in the energy spectrum of the system under consideration.

KEY WORDS: Master equations; time asymptotics; bound states; irreversibility.

One of the aims of nonequilibrium statistical mechanics is the description of the long-time behavior of a macroscopic system, i.e., the problem of irreversibility. One of the approaches is the investigation of the asymptotic properties of exact master equations. Presently, the best known of these is the so-called subdynamics of the Brussels School,[1–3] in which the asymptotic properties are introduced by means of assumptions about the analytical properties of some kinetic superoperators. The latter depend, among others, on the presence or the absence of bound states in the energy spectrum of the system under consideration.[4]

We found it convenient to study the convolutionless formalism of Fuliński.[5] In this formalism one begins with the Newmann–Liouville equation of motion ($\hbar = 1$):

$$\dot{\rho}(t) = -iL\rho(t) \tag{1}$$

where $\rho(t)$ is the density matrix and L is the Liouville superoperator generated by the Hamiltonian $\hat{H}$. The product of two superoperators, $K'K$,

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such that

$$K'K = 1 \tag{2}$$

is inserted into Eq. (1) and the result is multiplied from the left by the Zwanzig projection superoperator D, such that

$$D\rho = \rho_d, \qquad D\hat{H} = \hat{H}_0, \qquad \rho = \rho_d + \rho_n, \qquad \hat{H} = \hat{H}_0 + \hat{H}_1 \tag{3}$$

With K and K' appropriately chosen, and with D commuting with time differentiation, an exact convolutionless master equation of the general form

$$\dot{\rho}_d(t) = U(t, t_0)\rho_n(t_0) + V(t, t_0)\rho_d(t_0) + W(t, t_0)\rho_d(t) \tag{4}$$

is obtained.

Equation (4) can be used as a starting point for investigating the asymptotic properties of the system. Under the assumptions, specified below, and with the choice of K and K', also specified below, Fuliński was able to cast Eq. (4) into a form such that, in the limit $t_0 \to -\infty$,

$$W(t) = \gamma W^0 + W'(t) \tag{5}$$

with W^0 symmetric:

$$W^0 = DL^2D, \qquad W^0_{kkll} = W^0_{kl} = W^0_{lk}, \qquad \sum_k W^0_{kl} = 0 \tag{6}$$

and

$$\lim_{t\to\infty} W'(t) = 0_+ \tag{7}$$

Hence, in the lapse of time, the exact master equation (4) attains the asymptotic form

$$\dot{\rho}_{kk}(t) = \sum_l W^0_{kl}[\rho_{ll}(t) - \rho_{kk}(t)] + \text{d.t.} \tag{8}$$

The inhomogeneous "destruction terms" contain initial information, and must be investigated separately for a given physical system.

One of the assumptions made in the derivation of the above result was that neither the unperturbed system (described by the Hamiltonian $\hat{H}_0$) nor the whole system (Hamiltonian $\hat{H}$) has bound states.

The aim of this note is to relax this assumption and show that the above result remains valid in the presence of bound states.

We denote Z_+, Z_-, Z'_+, Z'_- (as in Refs. 5 and 6) by

$$\begin{aligned} Z_+ &= \lim_{t_0\to-\infty} Z(0, t_0)e^{-it_0L_0}, \qquad & Z_- &= \lim_{t\to+\infty} e^{itL_0}Z(t, 0) \\ Z'_+ &= \lim_{t_0\to-\infty} e^{it_0L_0}Z(t_0, 0), \qquad & Z'_- &= \lim_{t\to+\infty} Z(0, t)e^{-itL_0} \end{aligned} \tag{9}$$

and assume that (i) $Z_{\pm}$ exist in the Gell-Mann Goldberger limit; (ii) the initial condition is specified by the quantity $\exp(it_0L_0)\rho(t_0) = \rho^0$, which is kept constant when $t_0 \to -\infty$; (iii) the Hamiltonian $\hat{H}$ of the system is time independent, hence L and $Z(t_1, t_2)$ commute; (iv) there exists a representation $\{|k\rangle\}$ in which $\hat{H}_0$ is diagonal, hence the Zwanzig identities ($DLD = 0$; $DL_0 = L_0D = 0$; $L_0\rho = [\hat{H}_0, \rho]$) hold; (v) $\hat{H}_0$ has no bound states but $\hat{H}$ does, hence

$$Z_+ Z'_+ = Z_- Z'_- = 1 - B \tag{10}$$

$$Z'_+ Z_+ = Z'_- Z_- = 1 \tag{11}$$

where B is the projection superoperator onto bound states.

Choosing

$$K = K(t) = 1 - \lambda D + F(t)DZ(t,0)Z_+ \tag{12}$$

where λ is a number and $F(t)$ is any superoperator independent of t_0, and under assumptions (ii) and (v), the Liouville equation (LE) can be written as

$$\dot{\rho}_d(t) = U(t,t_0)\rho_n^0 + V(t,t_0)\rho_d^0 + W(t)\rho_d(t) + X(t,t_0)\rho^0 \tag{13}$$

where

$$U(t,t_0) = V(t,t_0) = -iDLZ(t,0)Z_+ K'(t)[1 - \lambda D]Z'_+ Z(0,t_0)e^{-it_0L_0} \tag{14}$$

$$W(t) = -iDLZ(t,0)Z_+ K'(t)F(t) \tag{15}$$

$$X(t,t_0) = -iDLZ(t,0)[1 - Z_+ K'(t)F(t)DZ(t,0)]BZ(0,t_0)e^{-it_0L_0} \tag{16}$$

Under assumptions (i) and (v) it can be found that

$$\lim_{t_0 \to -\infty} U(t,t_0) = -iDLZ(t,0)Z_+ K'(t)(1 - D) = U(t) \tag{17}$$

$$\lim_{t_0 \to -\infty} V(t,t_0) = -i(1-\lambda)DLZ(t,0)Z_+ K'(t)D = V(t) \tag{18}$$

$$\lim_{t_0 \to -\infty} X(t,t_0) = -iDLZ(t,0)[1 - Z_+ K'(t)F(t)DZ(t,0)]BZ_+ = X(t) \tag{19}$$

From assumption (v), and using $B^2 = B$, it follows that

$$BZ_+ = 0 \tag{20}$$

i.e.,

$$X(t) = 0$$

From these results the asymptotic expression for $\dot{\rho}_d(t)$ is

$$\lim_{t_0 \to -\infty} \dot{\rho}_d(t) = U(t)\rho_n^0 + V(t)\rho_d^0 + W(t)\rho_d(t) \tag{21}$$

which has the same form as the one obtained in Ref. 5 under the assumption that $\hat{H}$ has no bound states.

Let

$$\begin{aligned} F(t) &= iZ'_+ Z^{-1}(t,0)\left[\gamma + LDA(t)\right]L \\ K'(t) &= 1 + \lambda' D - E - \lambda ED \\ E(t) &= F(t)DZ(t,0)Z_+, \qquad \lambda' = \frac{\lambda}{1-\lambda}, \quad \lambda \neq 1, \quad \lambda' \neq 1 \end{aligned} \tag{22}$$

with γ and λ numbers and $A(t)$ any superoperator independent of t_0 and of B, it is easy to check that (22) and (12) indeed give $K'K = 1$. Inserting (22) into (17)–(21) one eventually[2] obtains the asymptotic master equation (8).[(5)]

This result indicates that the bound states of the nondiagonal part of the Hamiltonian do not change the asymptotic form of the LE.

In order to examine the effect of the bound states of $\hat{H}_0$ on the asymptotic form of the LE we assume from now on (v′) that both $\hat{H}$ and $\hat{H}_0$ have bound states, so instead of Eq. (11) we have

$$Z'_+ Z_+ = Z'_- Z_- = 1 - B_0 \tag{23}$$

with B_0 being the projection superoperator onto bound states of $\hat{H}_0$.

Using the form (12) for $K(t)$ and using assumptions (ii) and (v′), the LE takes the form (13) with the coefficients given by (14), (15), and (16), respectively.

Under assumptions (i) and (v′) we find that

$$\lim_{t_0 \to -\infty} U(t,t_0) = U(t) + iDLZ(t,0)Z_+ K'(t)(1 - \lambda D)B_0 \tag{24}$$

$$\lim_{t_0 \to -\infty} V(t,t_0) = V(t) + iDLZ(t,0)Z_+ K'(t)(1 - \lambda D)B_0 \tag{25}$$

and

$$\lim_{t_0 \to -\infty} X(t,t_0) = X(t) \tag{26}$$

where $U(t)$, $V(t)$, and $X(t)$ are defined by (17), (18), and (19), respectively.

Using (v′), one obtains

$$BZ_+ = Z_+ B_0 \tag{27}$$

Combining (24), (25), (26), and (27) we get the asymptotic expression of

[2] Note that the superoperators (22) (i) do not depend on t_0 and (ii) do not contain products of the type of (10), (11), or (23).

$\dot{\rho}_d(t)$ as

$$\lim_{t_0 \to -\infty} \dot{\rho}_d(t) = U(t)\rho_n^0 + V(t)\rho_d^0 + W(t)\rho_d(t) - iDLZ(t,0)Z_+ K'(t)(\lambda D - 1)B_0\rho^0 - iDLZ(t,0)\left[Z_+ - Z_+ K'(t)F(t)DZ(t,0)Z_+\right]B_0\rho^0 \quad (28)$$

The expression in the brackets, in the last term of (28), can be written as

$$Z_+ K'(t)K(t) - Z_+ K'(t)F(t)DZ(t,0)Z_+ \quad (29)$$

where $K'(t)K(t) = 1$ has been used.

Finally, the last two terms in (28) cancel each other out, as can be seen at once from (12), (28), and (29), thus once more we recover the relation (21), and hence the asymptotic form (8). The assumption that neither $\hat{H}_0$ nor $\hat{H}$ have bound states, made in the derivation of (8) in Ref. 5, then becomes unnecessary.

Our results show that the existence of bound states, either in the nondiagonal or in the diagonal part of the Hamiltonian of the system, does not change the asymptotic form of the Liouville equation.

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REFERENCES

1. I. Prigogine, C. George, and F. Henin, *Physica* **45**:418 (1969).
2. A. Grecos, T. Guo, and W. Guo, *Physica* **80A**:421 (1975).
3. E. Chen, *J. Math. Phys.* **17**:1785 (1976).
4. C. C. Chiang, *Nuovo Cimento* **25B**:125 (1975).
5. A. Fuliński, *Physica* **92A**:198 (1978).
6. A. Fuliński and C. Jedrzejek, *Phys. Lett.* **61A**:361 (1977).