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Statistical Mechanical Transformation Theory for Quantum Systems with Discrete Spectra

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The superoperator transformation theory developed by the Brussels school is applied to quantum systems with discrete spectra. In the case of nondegeneracy of the spectra, there is no difficulty in obtaining explicit expressions for the most important superoperators in terms of the unitary operator which diagonalizes the Hamiltonian. The degenerate case presents special problems which are studied in detail.

KEY WORDS: Discrete spectrum; superoperator transformation; asymptotic kinetic equation; dressing operator.

1. INTRODUCTION

In recent work in nonequilibrium statistical mechanics, a transformation theory has been developed for the Liouville–von Neumann equation in terms of "superoperators" which act on the density matrix.[1,2,11] These superoperators have been extensively studied within the context of the perturbative approach of the Brussels school in several papers, to which reference can be found in Refs. 2,11. It is perhaps appropriate to give a short resume of how these operators appear in statistical mechanics.

The mechanics of a system in the superoperator formalism are expressed in terms of operators acting on the Hilbert–Schmidt space $\mathscr{L}$ of density matrices. We solve the Liouville–von Neumann equation

$$i\,\partial\rho/\partial t = \mathsf{L}\rho \qquad \text{for} \quad \rho \in \mathscr{L}$$

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by means of the resolvent operator $(z - \mathsf{L})^{-1}$ of the Liouville operator L to obtain

$$\rho(t) = \mathsf{U}(t)\,\rho(0) = (1/2\pi i) \int_C e^{-izt}(z - \mathsf{L})^{-1}\,\rho(0)\,dz$$

where C is the Bromwich contour parallel to the real axis of z and above all singularities of the integrand. In some suitably chosen representation, the above equation is applied separately to the diagonal part, ρ_0, say, of the density matrix and the off-diagonal part ρ_ν.
The perturbative development of this equation in terms of the basic collision operator $\psi(z)$ and associated irreducible operators (see Ref. 1) yields the approximate long-time solution $\bar{\rho}(t)$ as follows:

$$\begin{pmatrix} \bar{\rho}_0(t) \\ \bar{\rho}_\nu(t) \end{pmatrix} = \begin{pmatrix} e^{-i\Omega\psi t}\mathsf{A} & e^{-i\Omega\psi t}\mathsf{AD} \\ \mathsf{C}e^{-i\Omega\psi t}\mathsf{A} & \mathsf{C}e^{-i\Omega\psi t}\mathsf{AD} \end{pmatrix} \begin{pmatrix} \rho_0(0) \\ \rho_\nu(0) \end{pmatrix}$$

This can be rewritten more compactly as

$$\bar{\rho}(t) = \Sigma(t)\,\rho(0)$$

where the superoperator Σ satisfies the semigroup property

$$\Sigma(t)\,\Sigma(t') = \Sigma(t + t'); \qquad t, t' \geqslant 0$$

Of particular interest is the limiting case

$$\Pi = \lim_{t\to 0+} \Sigma(t)$$

From the above, Π is a projection operator which can be written

$$\Pi = \begin{pmatrix} \mathsf{A} & \mathsf{AD} \\ \mathsf{CA} & \mathsf{CAD} \end{pmatrix}$$

The semigroup property of $\Sigma(t)$ and idempotent property of Π are equivalent to, and generally proved via, the identity

$$\mathsf{A}^2 + \mathsf{AD} \cdot \mathsf{CA} = \mathsf{A}$$

linking the basic operators of the theory (see Ref. 3).

The asymptotic diagonal part of ρ is given by

$$\bar{\rho}_0(t) = e^{-i\Omega\psi t}\mathsf{A}(1 + \mathsf{D})\,\rho(0) = e^{-i\Omega\psi t}\bar{\rho}_0(0)$$

It is interesting to look for a transformation which will render the generator of the evolution operator Hermitian. Accordingly, we introduce a superoperator X and consider

$$\tilde{\rho}_0(t) \equiv \mathsf{X}^{-1}\bar{\rho}_0(t) = [\exp(-i\mathsf{X}^{-1}\Omega\psi\mathsf{X}t)]\,\tilde{\rho}_0(0)$$

It has been shown[1] that $\mathsf{X}^{-1}\Omega\psi\mathsf{X}$ is Hermitian if X is any operator such that $\mathsf{XX}^\dagger = \mathsf{A}$ ($\mathsf{X}^\dagger$ being the Hermitian conjugate of X). A superoperator X satifying this and certain subsidiary conditions can be calculated order by order from a perturbation series and, on the basis of this, it has been suggested[4,9] by Mandel and Turner that such a X satisfies the equation, in terms of a coupling parameter λ:

$$\partial \mathsf{X}/\partial\lambda = -\mathsf{AD}(\partial \mathsf{C}/\partial\lambda)\,\mathsf{X}.$$

It is important for the understanding of the significance of the above superoperators to have explicit representations of them in simple cases; and this is most easily achieved in certain problems for which nonperturbative quantum mechanical solutions are available.

To this end, we consider quantum systems described by a Hamiltonian

$$H = H_0 + \lambda H_1$$

where the spectra of both H_0 and H are assumed to be discrete, and the spectrum of H is further taken to have no finite limit point, that is, there is to be a positive lower bound on the differences $|E_n - E_m|$, say, between the distinct eigenvalues of H. This latter requirement is not satisfied, for example, by the bound states of the hydrogen atom. For systems which do satisfy the above conditions, there exists a unitary transformation U which makes $H_D = UHU^{-1}$ diagonal in the basis of eigenvectors of H_0. Thus, if one represents the eigenvectors of H_0 by $|n\rangle, n = 0, 1,...,$ then

$$H_D\,|n\rangle = E_n\,|n\rangle$$

where the E_n are the eigenvalues of H. In terms of the eigenvectors $|\phi_n\rangle$, say, of H, the operator is given by

$$U = \sum_n |n\rangle\langle\phi_n| \tag{1}$$

For simplicity at the moment, H and H_0 will be assumed each to have a nondegenerate spectrum, although this requirement will be relaxed later. In accord with the usual practice, the diagonal elements of H_0 in the representation of the $|n\rangle$ will be chosen equal to those of H.

If ρ belongs to $\mathscr{L}$, we introduce the superoperator V by

$$\mathsf{V}\rho = U\rho U^{-1} \tag{2}$$

where U is the unitary transformation (1). With the usual scalar product on $\mathscr{L}$

$$(\rho_1, \rho_2) = \mathrm{Tr}\, \rho_1^{\dagger}\rho_2$$

it is easily seen that V is a unitary operator. The mechanics in $\mathscr{L}$ are generated by the Liouville–von Neumann operator L, defined by the relation

$$\mathsf{L}\rho = [H, \rho]$$

The operator VLV^{-1} can be written explicitly in the $|n\rangle$–representation:

$$\mathsf{VLV}^{-1}\rho = U[H, U^{-1}\rho U]\,U^{-1} = [H_D, \rho]$$

and

$$\langle m \mid \mathsf{VLV}^{-1}\rho \mid n\rangle = (E_m - E_n)\langle m \mid \rho \mid n\rangle \tag{3}$$

for any ρ in $\mathscr{L}$. This result essentially solves the dynamical problem in $\mathscr{L}$, since the time development of a density matrix ρ is given by

$$\begin{aligned}\rho(t) &= (1/2\pi i) \int_C e^{-izt}(z - \mathsf{L})^{-1}\, \rho(0)\, dz \\ &= (1/2\pi i)\, \mathsf{V}^{-1} \int_C e^{-izt}(z - \mathsf{VLV}^{-1})^{-1}\, \mathsf{V}\rho(0)\, dz\end{aligned} \tag{4}$$

The expression (4) can be made explicit with the aid of equation (3). We shall require a third basic superoperator P which maps a matrix ρ in $\mathscr{L}$ into the matrix consisting only of the diagonal elements of ρ in the $\mid n\rangle$-representation:

$$\langle m \mid \mathsf{P}\rho \mid n\rangle = \langle n \mid \rho \mid n\rangle\, \delta_{m,n} \tag{5}$$

It is simply verified that P is a projection operator.

In the next section, we examine and obtain explicit expressions for the long-time or asymptotic operators in the general theory, for the case of nondegenerate spectra.

In Section 3, the matter of inverse operators is discussed, and it is shown that the assumption that these exist leads to the usual equations of the general theory. The difficulties which appear when the spectrum is degenerate are pointed out in Section 4, where a method is suggested to overcome these.

2. ASYMPTOTIC OPERATORS

The general theory of Ref. 2 gives a prescription which yields the approximate density matrix $\bar{\rho}$ to describe the long-time behavior of a statistical system (in this case, it will be the ergodic average):

$$\bar{\rho}(t) = \Sigma(t)\, \rho(0) = (1/2\pi i) \int_{\gamma_0} e^{-izt}(z - \mathsf{L})^{-1}\, \rho(0)\, dz$$

where γ_0 is a contour obtained by closing the Bromwich contour C about the point $z = 0$ excluding all other singularities of the integrand. Our assumption that the eigenvalue differences $\mid E_n - E_m \mid$ have a positive lower bound implies that $z = 0$ is not a limit point of the spectrum of L, and so the contour γ_0 is well-defined and encloses only the zero eigenvalue of L. From this, it follows at once that $\bar{\rho}(t)$ is in fact independent of t, that is,

$$\bar{\rho}(t) = \bar{\rho}(0) = \Sigma(0)\, \rho(0) = \Pi\rho(0) \tag{6}$$

where

$$\Pi = (1/2\pi i) \int_{\gamma_0} (z - \mathsf{L})^{-1}\, dz$$

The operator Π is the projection operator onto the null space of L (just as P is for L_0, the Liouville operator corresponding to H_0) and it projects out the constant part of ρ. A more revealing expression for this operator can be found as follows:

$$\Pi = (1/2\pi i) \int_{\gamma_0} (z - \mathsf{L})^{-1}\, dz = (1/2\pi i)\, \mathsf{V}^{-1} \int_{\gamma_0} (z - \mathsf{VLV}^{-1})^{-1}\mathsf{V}\, dz$$

The interchange of the operations V^{-1} and $\int_{\gamma_0}$ is admissible here since V^{-1} is unitary and hence bounded and since $(z - \mathsf{VLV}^{-1})^{-1}$ is well-defined and bounded for z on γ_0. Now, from Eq. (3) there results

$$\langle m \,|(z - \mathsf{VLV}^{-1})^{-1}\, \rho \mid n\rangle = \{1/[z - (E_m - E_n)]\}\langle m \mid \rho \mid n\rangle$$

and thus

$$\langle m \mid (1/2\pi i) \int_{\gamma_0} dz (z - \mathsf{VLV}^{-1})^{-1}\rho \mid n\rangle = \langle n \mid\rho\mid n\rangle\, \delta_{m,n} \tag{7}$$

This shows that

$$(1/2\pi i) \int_{\gamma_0} dz\, (z - \mathsf{VLV}^{-1})^{-1} = \mathsf{P} \tag{8}$$

the projection operator defined by Eq. (5). In this way we obtain the very useful relation

$$\Pi = \mathsf{V}^{-1}\mathsf{PV} \tag{9}$$

It is useful at this point to introduce the projection operators $\mathsf{Q} = 1 - \mathsf{P}$ and $\hat{\Pi} = \mathsf{V}^{-1}\mathsf{QV}$ with the properties

$$\mathsf{Q}^2 = \mathsf{Q}, \qquad \hat{\Pi}^2 = \hat{\Pi}, \qquad \mathsf{QP} = \mathsf{PQ} = 0, \qquad \Pi\hat{\Pi} = \hat{\Pi}\Pi = 0$$

all four projectors being self-adjoint. It is convenient from the point of view of the general theory[2,11] to decompose the operator Π into four parts, conventionally labeled as follows:

$$\begin{aligned} \mathsf{A} &= \mathsf{P}\Pi\mathsf{P} = \mathsf{PV}^{-1}\mathsf{PVP}; &\qquad \mathsf{AD} &= \mathsf{P}\Pi\mathsf{Q} = (\mathsf{CA})^{\dagger} \\ \mathsf{CA} &= \mathsf{Q}\Pi\mathsf{P}; & \mathsf{CAD} &= \mathsf{Q}\Pi\mathsf{Q} \end{aligned} \tag{10}$$

As regards this notation, it is not obvious at this stage that CA, for example, is the product of A with another operator C. However, as discussed later, in Section 3, when the inverse operator A^{-1} exists, the operators C and D are well-defined. Since, for the moment, C and D will not occur other than in these expressions, the symbols CA, AD, CAD may be considered just as complicated labels for the three operators defined by Eqs. (10). The identity involving these operators,

$$\mathsf{A} = \mathsf{A}^2 + \mathsf{AD} \cdot \mathsf{CA}$$

which is widely used in the general theory (see, for example, Ref. 3), can be proved using our definitions (10):

$$\begin{aligned} \mathsf{A}^2 + \mathsf{AD} \cdot \mathsf{CA} &= \mathsf{P}\Pi\mathsf{P}\Pi\mathsf{P} + \mathsf{P}\Pi\mathsf{Q}\Pi\mathsf{P} \\ &= \mathsf{P}\Pi^2\mathsf{P} = \mathsf{P}\Pi\mathsf{P} = \mathsf{A} \end{aligned} \tag{11}$$

A further important use[1] of A in the general theory is to express the evolution of the diagonal elements of the asymptotic density matrix $\bar{\rho}$ when the initial density matrix is a purely diagonal $\rho_0(0)$:

$$\bar{\rho}_0(t) \equiv \mathsf{P}\bar{\rho}(t) = e^{-it\Omega\psi}\mathsf{A}\rho_0(0)$$

In view of Eq. (6), this shows that for the special systems under consideration

$$\Omega\psi\mathsf{A} = 0 \tag{12}$$

The operator A has an attractive factorization property. Among operators X such that $\mathsf{A} = \mathsf{X}\mathsf{X}^\dagger$, one possible choice is obvious from Eq. (10):

$$\mathsf{X} = \mathsf{P}\mathsf{V}^{-1}\mathsf{P} \tag{13}$$

Other choices can be obtained from this by multiplying on the right by an arbitrary unitary superoperator. However, the operator X of Eq. (13) is of special interest since it has the further property

$$\mathsf{X}H_D = H_0 \tag{14}$$

This can be seen readily in the $| n\rangle$-representation:

$$\langle l \mid \mathsf{X}H_D \mid k\rangle = 0 \qquad \text{if} \quad l \neq k$$

$$\langle l \mid \mathsf{X}H_D \mid l\rangle = \sum_{kk'mn} \langle l \mid U^{-1} \mid k\rangle\langle k \mid U \mid m\rangle\langle n \mid U^{-1} \mid k'\rangle\langle k' \mid U \mid l\rangle\langle m \mid H \mid n\rangle$$

$$= \langle l \mid H \mid l\rangle = \langle l \mid H_0 \mid l\rangle$$

from Eqs. (2), (5), and (13).

This factorization of A immediately suggests that one apply the same argument to Π itself, for which

$$\Pi = \mathsf{V}^{-1}\mathsf{P}\mathsf{V} = (\mathsf{V}^{-1}\mathsf{P})(\mathsf{V}^{-1}\mathsf{P})^\dagger = (\mathsf{P}\mathsf{V})^\dagger\,(\mathsf{P}\mathsf{V})$$

The operator PV is called $\bar{\gamma}$ by Mandel[4] and is used extensively in his analysis of transformation theories. By using explicitly the fact that V is the diagonalizing transformation for H, and a version of the Hellman–Feynman theorem, he has shown in the paper quoted that $\bar{\gamma}$ satisfies

$$\partial\bar{\gamma}/\partial\lambda = \bar{\gamma}\,\partial\Pi/\partial\lambda \tag{15}$$

which is equivalent to the Mandel–Turner equation, as shown in Section 3.

This result may easily be proved in the present notation by using the Hellman–Feynman theorem in the form

$$\mathsf{P}\mathsf{V}(\partial\mathsf{V}^{-1}/\partial\lambda)\,\mathsf{P}\rho = 0$$

for any ρ in $\mathscr{L}$, which is verified most simply by taking matrix elements.

We conclude this section by giving component elements for some of the more important superoperators in terms of the matrix elements of U. From Eq. (9),

$$\langle i \mid \Pi\rho \mid j\rangle = \sum_{mkl} \langle m \mid U \mid i\rangle^* \langle m \mid U \mid j\rangle \langle m \mid U \mid k\rangle \langle m \mid U \mid l\rangle^* \langle k \mid \rho \mid l\rangle$$

where the asterisk denotes a complex conjugate. This can be written in the tetradic form

$$\langle ij \mid \Pi \mid kl\rangle = \sum_{m} \langle m \mid U \mid i\rangle^* \langle m \mid U \mid j\rangle \langle m \mid U \mid k\rangle \langle m \mid U \mid l\rangle^* \tag{16}$$

In the same notation,

$$\langle ij \mid \mathsf{A} \mid kl\rangle = \delta_{ij}\delta_{kl} \sum_{m} |\langle m \mid U \mid i\rangle|^2 \, |\langle m \mid U \mid k\rangle|^2 \tag{17}$$

and

$$\langle ij \mid \mathsf{X} \mid kl\rangle = \delta_{ij}\,\delta_{kl}\, |\langle k \mid U \mid i\rangle|^2 \tag{18}$$

These expressions will be useful in Section 3.

3. THE INVERSE OPERATORS

It is important for the general theory[1] that the inverse operators A^{-1}, X^{-1} exist. They are needed both for the physical interpretation of the theory and for the justification of writing the equations (10) in the form given and regarding the operators C and D as well-defined. We examine this question here, and concentrate on the operator X, since the existence of X^{-1} implies that of A^{-1}. For simplicity, only the nondegenerate case will be considered in this section.

The superoperator X was introduced in Eq. (13) as

$$\mathsf{X} = \mathsf{P}\mathsf{V}^{-1}\mathsf{P}$$

which is not a useful form for present purposes. The presence of the projector P renders it virtually impossible to make any general statement on the existence of an inverse. Fortunately, we have an explicit matrix representation of X which can be obtained from Eq. (18). The elements of X which are not trivially zero can be written as a matrix with elements

$$\begin{aligned} \langle i \mid \mathsf{X} \mid j\rangle &\equiv \langle ii \mid \mathsf{X} \mid jj\rangle \\ &= |\langle j \mid U \mid i\rangle|^2 \end{aligned} \tag{19}$$

From this form, it is clear that the existence of X^{-1} is not automatic, since it is simple to construct unitary operators U which lead to a singular matrix for X which accordingly has no inverse. Thus, it must be made as a separate assumption that for most systems of physical interest the inverse operator exists, and then this matter should be verified for each example individually. (A simple case is treated in a forthcoming paper by the authors.[8])

If it is assumed that X^{-1} does indeed exist, some of its properties can now be examined. By Eq. (19), the matrix for X has only nonnegative elements, and further, since U is unitary,

$$\sum_i \langle i \mid \mathsf{X} \mid j\rangle = 1 = \sum_j \langle i \mid \mathsf{X} \mid j\rangle \tag{20}$$

X is therefore a doubly stochastic matrix with all its elements less than or equal to unity. X^{-1} also satisfies the relation (20), but cannot have the property that all its elements lie in the interval [0, 1] unless all these elements are either zero or unity. In fact, except in this latter case, the identity

$$\sum_j \langle i \mid \mathsf{X} \mid j\rangle\langle j \mid \mathsf{X}^{-1} \mid k\rangle = \delta_{ik} \tag{21}$$

shows that for each k at least one of the $\langle j \mid \mathsf{X}^{-1} \mid k\rangle, j = 0, 1,...,$ is negative, and further, that for each k, at least one choice of j gives $\langle j \mid \mathsf{X}^{-1} \mid k\rangle > 1$. The first of these remarks follows at once from Eq. (21) by choosing any i different from k. For the second, suppose on the contrary that $\langle j \mid \mathsf{X}^{-1} \mid k\rangle \leqslant 1$ for every j and let the positive matrix elements be labeled by $j \in I$, and the negative ones by $j \in J$. Then,

$$\begin{aligned}
1 &= \sum_j \langle k \mid \mathsf{X} \mid j\rangle\langle j \mid \mathsf{X}^{-1} \mid k\rangle \\
&= \sum_{j\in I} \langle k \mid \mathsf{X} \mid j\rangle\langle j \mid \mathsf{X}^{-1} \mid k\rangle - \sum_{j\in J} \langle k \mid \mathsf{X} \mid j\rangle \, |\langle j \mid \mathsf{X}^{-1} \mid k\rangle| \\
&\leqslant \sum_{j\in I} \langle k \mid \mathsf{X} \mid j\rangle - \sum_{j\in J} \langle k \mid \mathsf{X} \mid j\rangle \, |\langle j \mid \mathsf{X}^{-1} \mid k\rangle| \\
&< \sum_{\text{all } j} \langle k \mid \mathsf{X} \mid j\rangle \\
&= 1
\end{aligned}$$

which is a contradiction.

As noted above, the existence of X^{-1} implies that of A^{-1} and since, by Eq. (17), A is a symmetric, doubly stochastic matrix, A^{-1} shares the above properties with X^{-1}.

These properties give rise to some interesting conclusions. In the general theory,

$$\tilde{\rho}_0(t) = \mathsf{X}^{-1}\bar{\rho}_0(t)$$

is regarded as the diagonal part of a "dressed" or "physical" density matrix obtained from an original "unphysical" ρ. From Eqs. (6) and (10),

$$\begin{aligned}
\tilde{\rho}_0(t) = \tilde{\rho}_0(0) &= \mathsf{X}^{-1}\mathsf{A}(1 + \mathsf{D})\,\rho(0) \\
&= \mathsf{X}^{\dagger}(1 + \mathsf{D})\,\rho(0)
\end{aligned}$$

If a pure state is chosen for $\tilde{\rho}$, the above properties of the inverses show that $(1 + \mathsf{D})\,\rho(0)$ has at least one negative element and at least one element greater than unity, which is impossible if $\mathsf{D}\rho = 0$. In particular, a pure state for $\tilde{\rho}$ can arise only from a $\rho(0)$ which has $\mathsf{Q}\rho(0) \neq 0$, i.e., the initial state must have correlations present.

When the operators A^{-1}, X^{-1} exist, the general theory can proceed in the usual way. The operators C and D of Eqs. (10) are well-defined, and the identity (11) gives at once

$$\mathsf{A}^{-1} = 1 + \mathsf{D} \cdot \mathsf{C}$$

Further, Eq. (12) now reduces to $\Omega\psi = 0$, whence $\psi = 0$. Finally, it is seen that the factorisation of Π can now be written

$$\Pi = \bar{\gamma}^{\dagger}\bar{\gamma} = (1 + \mathsf{C})\,\mathsf{X}\mathsf{X}^{\dagger}(1 + \mathsf{D})$$

whence

$$\bar{\gamma} = \mathsf{X}^{\dagger}(1 + \mathsf{D}) \tag{22}$$

If we decompose all superoperators in the fashion of Eqs. (10) and write the components as a 2×2 matrix of operators, then, with the help of the result (22), the two sides of Eq. (15) may be written as follows:

$$\partial\bar{\gamma}/\partial\lambda = \begin{pmatrix} \partial\mathsf{X}^{\dagger}/\partial\lambda & \partial\mathsf{X}^{\dagger}\mathsf{D}/\partial\lambda \\ 0 & 0 \end{pmatrix}$$

and

$$\bar{\gamma}\,\partial\Pi/\partial\lambda = \begin{pmatrix} \mathsf{X}^{\dagger}\dfrac{\partial\mathsf{A}}{\partial\lambda} + \mathsf{X}^{\dagger}\mathsf{D}\dfrac{\partial}{\partial\lambda}(\mathsf{CA}) & \mathsf{X}^{\dagger}\dfrac{\partial}{\partial\lambda}(\mathsf{AD}) + \mathsf{X}^{\dagger}\mathsf{D}\dfrac{\partial}{\partial\lambda}(\mathsf{CAD}) \\ 0 & 0 \end{pmatrix}$$

Hence, Eq. (15) is equivalent to :

$$\partial\mathsf{X}^{\dagger}/\partial\lambda = \mathsf{X}^{\dagger}(\partial\mathsf{A}/\partial\lambda + \mathsf{D}\partial[\mathsf{CA}]/\partial\lambda)$$

or else, since $\mathsf{X}^{\dagger} = \mathsf{X}^{-1}\mathsf{A}$,

$$\partial\mathsf{X}^{-1}/\partial\lambda = \mathsf{X}^{-1}\mathsf{AD}\;\partial\mathsf{C}/\partial\lambda$$

In this form, the result is usually called the Mandel–Turner equation.[9]

4. THE DEGENERATE CASE

In this section, we shall examine the extra difficulties which arise in an attempt to treat degenerate systems by the methods of Section 2. Thus, we now admit the possibility that different eigenfunctions $| E_i^0 m_i\rangle$ say, of H_0 may correspond to the same eigenvalue E_i^0, and different eigenfunctions $| E_j n_j\rangle$ of H to the same eigenvalue E_j.

The first place where a difficulty occurs is in the defining equation (5) for P. This definition as it stands would suffice for the purposes of this paper, but from the point of view of the general theory, in particular with regard to the perturbation expansion of Ref. 1, it must be changed somewhat. An examination of this perturbative scheme reveals that a useful P should have the following properties:

$$\mathsf{PL}_0 = \mathsf{L}_0\mathsf{P} = 0 \tag{23}$$

$$\mathsf{PLP} = 0 \tag{24}$$

$$(z - \mathsf{L}_0)^{-1}\,\mathsf{Q}\rho \quad \text{contains no terms proportional to} \quad z^{-1} \tag{25}$$

The first two conditions (23) and (24) are satisfied by the definition (5), but not the "irreducibility" condition (25) when H_0 is degenerate.

This last condition, however, is necessary for the usual perturbation expansion to have the meaning ascribed to it in the derivation of the generalized master equation. It can be noted that in order to satisfy condition (25) it is necessary and sufficient that the projected space $\mathsf{P}\mathscr{L}$ be the entire null space of L_0, that is, that P be defined by

$$\begin{aligned} \langle E_i^0 m_i \mid \mathsf{P}\rho \mid E_j^0 n_j\rangle &= 0 \qquad \text{if} \quad i \neq j \\ \langle E_i^0 m_i \mid \mathsf{P}\rho \mid E_i^0 n_i\rangle &= \langle E_i^0 m_i \mid \rho \mid E_i^0 n_i\rangle \end{aligned} \tag{26}$$

However, this choice of P does not in general satisfy condition (24), so that in the operators used above and in any kinetic equations derived in terms of them, explicit account must be taken of the operator PLP. (This is akin to a difficulty in treating spatially inhomogeneous classical systems.[5]) A way to avoid this difficulty is to modify the decomposition of H as $H_0 + \lambda H_1$, along lines suggested by the methods of degenerate perturbation theory in quantum mechanics, in such a way that P can be constructed to satisfy all three conditions (23)–(25). The first step is to proceed from the basis $\mid E_i^0 m_i\rangle$ in each degenerate subspace to a new orthonormal basis $\mid E_i^0 \alpha_i\rangle$ which has the property $\langle E_i^0 \alpha_i \mid H_1 \mid E_i^0 \beta_i\rangle = 0$ unless $\alpha_i = \beta_i$.[6] A new decomposition $H = H_0' + \lambda H_1'$ is now made, where H_0' is the diagonal part of H in the new basis:

$$\langle E_i^0 \alpha_i \mid H_0' \mid E_j^0 \beta_j\rangle = \delta_{ij}\delta_{\alpha_i\beta_i}[E_i^0 + \langle E_i^0 \alpha_i \mid \lambda H_1 \mid E_i^0 \alpha_i\rangle]$$

and where H_1' accordingly satisfies:

$$\langle E_i^0 \alpha_i \mid H_1' \mid E_j^0 \beta_j\rangle = 0 \qquad \text{if} \quad i = j$$

If we further assume that the change of basis has introduced no further degeneracy in H_0', that is, if the equality

$$E_i^0 + \langle E_i^0 \alpha_i \mid \lambda H_1 \mid E_i^0 \alpha_i\rangle = E_j^0 + \langle E_j^0 \beta_j \mid \lambda H_1 \mid E_j^0 \beta_j\rangle$$

implies that $i = j$, then we can define a projector P which projects onto the entire null space of the superoperator $\mathsf{L}_0' = [H_0', ...]$:

$$\langle E_i^0 \alpha_i \mid \mathsf{P}\rho \mid E_j^0 \beta_j\rangle = \delta_{ij}\langle E_i^0 \alpha_i \mid \rho \mid E_j^0 \beta_j\rangle$$

if

$$\langle E_i^0 \alpha_i \mid \lambda H_1 \mid E_i^0 \alpha_i\rangle = \langle E_j^0 \beta_j \mid \lambda H_1 \mid E_j^0 \beta_j\rangle$$

and is equal to zero otherwise. It is easy to verify that P defined in this way satisfies the three conditions (23)–(25) with L_0 replaced by L_0'.

The second place where a difference occurs between degenerate and nondegenerate cases is Eq. (8), which need no longer be valid. A degeneracy in H_0 as treated above affects the complexity of calculation but cannot, of course, affect the final answers. A degeneracy in H is another matter and leads to the breakdown of Eq. (8). Since notation can be a problem here, we revert to labeling the eigenvectors of H_0 (or H_0', as the case may be) by $| n\rangle$ and shall say that $| n\rangle$ *belongs to* E_i, an eigenvalue of H, if

$$UHU^{-1} | n\rangle = E_i | n\rangle$$

Each $| n\rangle$ thus belongs to some E_i, but if H is degenerate, more than one $| n\rangle$ may belong to a given E_i. In this latter case, Eq. (7) should be replaced by

$$\langle m | (1/2\pi i) \int_{\gamma_0} dz(z - \mathsf{VLV}^{-1})^{-1}\rho | n\rangle = \langle m | \rho | n\rangle$$

provided that $| m\rangle$ and $| n\rangle$ belong to the same E_i, and zero otherwise. A new projection operator S may be defined:

$$\mathsf{S} = (1/2\pi i) \int_{\gamma_0} (z - \mathsf{VLV}^{-1})^{-1}\, dz \tag{27}$$

which in general need not be related to P. Analogously to Eq. (9) there results

$$\Pi = \mathsf{V}^{-1}\mathsf{SV} \tag{28}$$

and the program must now be developed in terms of two projectors P and S. If H is nondegenerate, then exactly one $| n\rangle$ belongs to each E_i, and S, as defined above, reduces to the diagonal projection given by Eq. (5). The operator X can still be defined as $\mathsf{PV}^{-1}\mathsf{S}$, and has the properties

$$\mathsf{XX}^\dagger = \mathsf{A} = \mathsf{P}\Pi\mathsf{P}$$

and

$$\mathsf{X}H_D = H_0'$$

since

$$\langle m | \mathsf{PV}^{-1}\mathsf{S}H_D | n\rangle = \sum_l \langle m | U^{-1} | l\rangle\langle l | H_D | l\rangle\langle l | U | n\rangle$$
$$= \langle m | H | n\rangle$$

provided that $| m\rangle$ and $| n\rangle$ both correspond to the same eigenvalue of H_0', and zero otherwise.

From the definition of H_0' then, this last quantity is just $\langle m | H_0' | n\rangle$. There remains, however, a point of difference from the nondegenerate case. Although we can define an operator $\bar{\gamma}$ in the same way as before, namely

$$\bar{\gamma} = \mathsf{SV}, \qquad \bar{\gamma}^\dagger\bar{\gamma} = \Pi$$

it need not in general satisfy Eq. (15). Indeed, if Eq. (15) holds, then necessarily

$$\mathsf{S}\mathsf{V}(\partial \mathsf{V}^{-1}/\partial\lambda)\,\mathsf{S} = 0$$

that is,

$$\sum_l [\langle m \mid U\,\partial U^{-1}/\partial\lambda \mid l\rangle\langle l \mid \rho \mid n\rangle - \langle m \mid \rho \mid l\rangle\langle l \mid U\,\partial U^{-1}/\partial\lambda \mid n\rangle] = 0 \qquad (29)$$

for $\mid m\rangle$, $\mid n\rangle$, $\mid l\rangle$ belonging to the *same* E_i and for arbitrary ρ in $\mathscr{L}$. This relation (29) clearly cannot be satisfied unless the states $\mid m\rangle$, $\mid n\rangle$, $\mid l\rangle$ are identical, which is the nondegenerate case considered in Section 2, or unless $U\,\partial U^{-1}/\partial\lambda$ is a multiple of the identity in each subspace spanned by the kets $\mid m\rangle$ belonging to a given eigenvalue. This latter condition will not hold generally, since there are simple physical systems for which it is untrue. An example is a two-dimensional isotropic quantum harmonic oscillator subject to a perturbing constant external field in a fixed direction. (For the operators required in this model, see Ref. 7.)

5. CONCLUSIONS

It is apparent that there is no difficulty in incorporating quantum systems with nondegenerate discrete spectra into the superoperator transformation theory. In the case of degeneracy in H_0, calculational difficulties can arise in the definition of a suitable projector P, but these may be overcome by making a new decomposition of H into H_0' and $\lambda H_1'$, according to the procedure described in Section 4.

Other problems, not so readily disposed of, appear when H itself is degenerate. In order to develop a sensible theory, it seems necessary to introduce two projection operators P and S and retain them throughout. This permits most, but not all, of the theory to proceed as before. The main difference is that the Mandel–Turner equation no longer seems to be generally valid. It emerges clearly from Section 3 that the existence of the inverse operators A^{-1} and X^{-1}, normally assumed in the general theory, is by no means immediate and must be established independently for each individual case. Further, the mere existence of the inverse operators gives rise to some interesting properties. It is interesting to see these appearing in a simple way without any use of approximation techniques. Similar features have occurred previously in the superoperator theory within the framework of perturbation theory (see Ref. 10, where they are discussed).

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