Formation of ensembles with constraints of coherence*

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We discuss the construction of the ensemble density matrix for a system for which off-diagonal elements (coherences) are known and thus are imposed constraints. The density matrix is determined according to maximization of the entropy subject to the imposed constraints. In contrast to the specification of diagonal density matrix elements, the specification of coherences has a significant influence on the unspecified density matrix elements. If the ensemble so formed serves as an initial condition, then the subsequent temporal evolution is affected by the initial specification of the coherences. Connections with experiments are indicated.

I. INTRODUCTION

The temporal evolution of a macroscopic system is dependent on the dynamics of the system (its Hamiltonian) and its initial (and boundary) conditions. The initial condition is determined by the experimental constraints imposed on the system prior to its evolution. The range of that specification of the initial condition may be limited. For a macroscopic system it is hardly possible (nor perhaps desirable) to fix all the elements of the initial density matrix. Usually we know certain averages of macroscopic observables, such as energy or magnetization. The characterization of the initial condition is then a statistical problem. We have to find the most probable density matrix consistent with the experimental constraints. Having partial information on a macroscopic system, the way to determine the most probable density matrix is to maximize the entropy $-\mathrm{Tr}\rho\ln\rho$ subject to the constraints of the experiment.[1-5] The assumptions of equal *a priori* probability and random phases are made in this procedure. The resultant density matrix[2] describes the most probable initial state.

Recent advances in experimental techniques,[6-8] however, have made it possible to fix some initial *elements* of the density matrix, in particular off-diagonal terms (coherences). The purpose of this article is to study the formation of statistical ensembles in such cases. In particular, we show the important influence of the specification of coherent density matrix elements as compared to diagonal elements.

II. DETERMINATION OF ENSEMBLES (DENSITY MATRICES) ACCORDING TO PRESCRIPTION OF MAXIMAL ENTROPY

We consider some examples of constraints on the initial condition of a system. In each case we maximize the entropy $S=-\mathrm{Tr}\rho\ln\rho$ subject to the stipulated constraints and thus determine the density matrix (operator).

First, for comparison, we analyze the trivial case for which certain probabilities (i.e., diagonal elements of the density matrix) are given. Such constraints have a very limited influence with respect to the construction of the whole probability distribution (or the whole density matrix). To see this, suppose that we are given the value of $\rho_{ii}=p_i$. We maximize the entropy

$$S=-\mathrm{Tr}\rho\ln\rho\ , \tag{1}$$

subject to the constraints

$$\mathrm{Tr}\rho=1\ ,\qquad \mathrm{Tr}(\rho|i\rangle\langle i|)=\rho_{ii}\ . \tag{2}$$

The resultant density matrix (see Appendix A) is

$$\rho=\exp[-\lambda_0-\lambda_1|i\rangle\langle i|]\ , \tag{3}$$

where λ_0 and λ_1 are Lagrange multipliers, to be calculated by using (2). The values of the probabilities p_j, $j\neq i$, and of ρ_{kl}, the off-diagonal elements of ρ, are

$$p_j=\langle j|\exp[-\lambda_0-\lambda_1|i\rangle\langle i|]|j\rangle\ , \tag{4}$$

$$\rho_{kl}=\langle k|\exp[-\lambda_0-\lambda_1|i\rangle\langle i|]|l\rangle\ . \tag{5}$$

Clearly, p_j is independent of j when $j\neq i$, and $\rho_{kl}=0$, for $k\neq l$. The maximal entropy prescription thus divides $1-p_i$ uniformly over all the accessible states, with no preference of any one state. Moreover, the prescription dictates a diagonal matrix, and no coherences are allowed.

Next we consider systems for which we specify in the initial condition some off-diagonal components of the density matrix (coherences). We show that, contrary to the above discussion, the knowledge of coherent elements is more decisive in the determination of the density matrix because they influence the values of *other* terms of the density matrix, both diagonal and off diagonal. We work out three typical examples. The first two deal with initial constraints consisting of specific diagonal and off-diagonal elements of the density matrix. The third example adds the condition of some average information, such as the mean energy of the system, in addition to the knowledge of some coherent terms.

Let us start with the simplest example. Suppose that we have a three-state system[9] designated $|a\rangle$, $|b\rangle$, and $|c\rangle$. We further suppose that at time $t=0$ some perturbation has been applied to the system which produces a coherence between the $|a\rangle$ and $|b\rangle$ states. In addition, we know one of the probabilities, say ρ_{aa}. Our problem is to construct the most probable density matrix that characterizes the system when the coherence is known. In the previous paragraph we demonstrated that without the coherent terms the principle of maximal entropy leads to a uniform division of $1-\rho_{aa}$ between ρ_{bb} and

ρ_{cc}. Now we show that the coherent terms change this situation.

We want to maximize

$$S = -\operatorname{Tr}\rho \ln\rho \tag{6}$$

subject to the constraints

$$\begin{aligned} &\operatorname{Tr}\rho = 1 ,\\ &\operatorname{Tr}\rho |a\rangle\langle a| = \rho_{aa} ,\\ &\operatorname{Tr}\rho |a\rangle\langle b| = \rho_{ba} ,\\ &\operatorname{Tr}\rho |b\rangle\langle a| = \rho_{ab} . \end{aligned} \tag{7}$$

In Appendix A we show that the density matrix operator which maximizes S is given by

$$\rho = \exp[-\lambda_0 - \lambda_a |a\rangle\langle a| - \lambda_{ab}|a\rangle\langle b| - \lambda_{ba}|b\rangle\langle a|] , \tag{8}$$

where λ_0, λ_a, λ_{ab}, and λ_{ba} are Lagrange multipliers to be determined by the set of equations (7). Equivalently, we can solve for the Lagrange multipliers by calculating the matrix elements, using Eq. (8):

$$\begin{aligned} &\langle a|\rho|a\rangle = \rho_{aa} ,\\ &\langle a|\rho|b\rangle = \rho_{ab} ,\\ &\langle b|\rho|a\rangle = \rho_{ba} ,\\ &\operatorname{Tr}\rho = 1 . \end{aligned} \tag{9}$$

In Appendix B we present a convenient method for the exact evaluation of the matrix elements of (8).[10,11] The method consists of defining a new operator $G(E)$ which is the Laplace transform of our operator (8), written in the form $\exp(At)$. The matrix elements of $G(E)$ can be easily evaluated using a Dyson-type equation. In this way the original problem is reduced to the solution of N systems of N algebraic equations, one for each row (or column) of $G(E)$. Later a contour integration[10] is used for inverting the Laplace transform and obtaining the matrix elements of $\exp(At)$. This method was recently applied to various molecular dynamics problems.[11]

First let us rewrite Eq. (8) in the form

$$\rho = \exp(-\lambda_0)\exp(-iAt) \tag{10}$$

where

$$A = -i\begin{pmatrix} \lambda_a & \lambda_{ab} & 0 \\ \lambda_{ba} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix} \tag{11}$$

and $t=1$. Next, we separate A into its diagonal and off-diagonal parts:

$$A = A_0 + A' , \tag{11'}$$

$$A_0 = -i\begin{pmatrix} \lambda_a & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \tag{11''}$$

$$A' = -i\begin{pmatrix} 0 & \lambda_{ab} & 0 \\ \lambda_{ba} & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}. \tag{11'''}$$

Making use of the Dyson equation (B4), we can now solve for the matrix elements of G. The results are

$$G_{aa} = \frac{E}{(E-iE^+)(E-iE^-)} , \tag{12a}$$

$$G_{ba} = \frac{-i\lambda_{ba}}{(E-iE^+)(E-iE^-)} , \tag{12b}$$

$$G_{ab} = \frac{-i\lambda_{ab}}{(E-iE^+)(E-iE^-)} , \tag{12c}$$

$$G_{bb} = \frac{E+i\lambda_a}{(E-iE^+)(E-iE^-)} , \tag{12d}$$

$$G_{cc} = G_{ca} = G_{ac} = G_{cb} = G_{bc} = 0 , \tag{12e}$$

where $iE^{\pm}$ are the solutions of

$$E^2 + i\lambda_a E + |\lambda_{ab}|^2 = 0 , \tag{13}$$

namely,

$$E^{\pm} = \tfrac{1}{2}(-\lambda_a \pm 2\gamma) , \tag{14}$$

where

$$\gamma = \tfrac{1}{2}(\lambda_a^2 + 4|\lambda_{ab}|^2)^{1/2} . \tag{14'}$$

With these equations we readily calculate the elements of the density matrix operator by carrying out the inverse Laplace transform (B2) and obtain

$$\rho = \exp(-\lambda_0) \cdot \begin{pmatrix} \frac{1}{2\gamma}\exp\left(-\frac{\lambda_a}{2}\right)[2\gamma\cosh\gamma - \lambda_a\sinh\gamma] & -\frac{\lambda_{ab}}{\gamma}\exp\left(-\frac{\lambda_a}{2}\right)\sinh\gamma & 0 \\ -\frac{\lambda_{ba}}{\gamma}\exp\left(-\frac{\lambda_a}{2}\right)\sinh\gamma & \frac{1}{2\gamma}\exp\left(-\frac{\lambda_a}{2}\right)[2\gamma\cosh\gamma + \lambda_a\sinh\gamma] & 0 \\ 0 & 0 & 1 \end{pmatrix}. \tag{15}$$

The following points need to be stressed:

(1) Hermiticity of ρ requires that $\lambda_{ab} = \lambda_{ba}^*$ and that λ_0 and λ_a be real. We note also the inequality $|\rho_{ab}| \le \sqrt{\rho_{aa}\rho_{bb}}$. On the other hand, λ_a can have any value between $-\infty$ and $+\infty$. In the limit $\lambda_{ab} \to 0$, we have

$$\begin{aligned} &\exp(-\lambda_0) = \frac{1-\rho_{aa}}{2} ,\\ &\exp(-\lambda_a) = \frac{2\rho_{aa}}{1-\rho_{aa}} , \end{aligned} \tag{16}$$

and thus

$$\lambda_a \to \begin{cases} \infty & \text{if } \rho_{aa} \to 0 \\ 0 & \text{if } \rho_{aa} \to \frac{1}{3} \\ -\infty & \text{if } \rho_{aa} \to 1\,. \end{cases} \tag{17}$$

(2) The unknown diagonal density matrix elements are no longer equipartitioned in this case. Equipartition between $|b\rangle$ and $|c\rangle$ is possible only if $\lambda_{ab}=0$, which holds when no coherent constraint (information) is given. The reason for this is that production of the coherence ρ_{ab} requires the application of some perturbation to the stationary system (where $\rho_{ab}=0$). This perturbation, which necessarily couples the $|b\rangle$ state to some other states, has to influence also the population ρ_{bb}. This effect is reflected in our density matrix, determined according to the maximization of entropy.

(3) In the present derivation we have assumed that ρ_{ab} is known. In practice, ρ_{ab} is a complex number and the available information may consist of only its real or imaginary parts. We could carry out the same derivation, replacing the term $\lambda_{ab}|a\rangle\langle b| + \lambda_{ba}|b\rangle\langle a|$ in the exponent Eq. (8) by $\lambda_{ab}(|a\rangle\langle b| + |b\rangle\langle a|)$ or $\lambda_{ab}(|a\rangle\langle b| - |b\rangle\langle a|)$, depending on whether we know $\mathrm{Re}\rho_{ab}$ or $\mathrm{Im}\rho_{ab}$, respectively. The resulting density matrix will have the same form as (15), and thus ρ_{ab} will be real or pure imaginary.

(4) Although the present example considered a three-level system, the result can be easily generalized to an n-level system where instead of $|c\rangle$ we have the states $|c\rangle$, $|d\rangle$, $|e\rangle$, ..., etc. Working along the same lines, the final result for ρ is the following:

(a) The upper left 2×2 matrix has the same form as (15).

(b) The submatrix of all other states ($|c\rangle$, $|d\rangle$, ...) for which we have no initial information has no off-diagonal elements.

(c) The states $|c\rangle$, $|d\rangle$, ... are equipartitioned:

$$\rho_{cc} = \rho_{dd} = \rho_{ee} = \cdots = \frac{1-\rho_{aa}-\rho_{bb}}{n-2}\,. \tag{18}$$

For the second example we choose constraints corresponding to the elements ρ_{aa}, ρ_{ab}, and ρ_{ac}, which are specified ($\rho_{ba}=\rho^*_{ab}$, $\rho_{ca}=\rho^*_{ac}$). In this case the density matrix determined by maximizing the entropy is

$$\rho = \exp[-\lambda_0 - \lambda_a|a\rangle\langle a| - \lambda_{ab}|a\rangle\langle b| - \lambda_{ba}|b\rangle\langle a| - \lambda_{ac}|a\rangle\langle c| - \lambda_{ca}|c\rangle\langle a|]\,. \tag{19}$$

Following the same arguments as in the previous example, we obtain the elements of $G(E)$, of which we list here only the diagonal ones:

$$G_{aa} = \frac{E}{(E-iE^+)(E-iE^-)}\,, \tag{20a}$$

$$G_{bb} = \frac{E(E+i\lambda_a)+|\lambda_{ac}|^2}{E(E-iE^+)(E-iE^-)}\,, \tag{20b}$$

$$G_{cc} = \frac{E(E+i\lambda_a)+|\lambda_{ab}|^2}{E(E-iE^+)(E-iE^-)}\,, \tag{20c}$$

where

$$E^{\pm} = \tfrac{1}{2}[-\lambda_a \pm 2\delta]\,, \qquad \delta = \tfrac{1}{2}(\lambda_a^2 + 4|\lambda_{ab}|^2 + 4|\lambda_{ac}|^2)^{1/2}\,. \tag{21}$$

Substituting $G(E)$ in (B2) and performing the integrations results in the matrix elements of ρ:

$$\rho = e^{-\lambda_0}\begin{pmatrix} \frac{1}{2\delta}\exp\left(-\frac{\lambda_a}{2}\right)[2\delta\cos\delta - \lambda_a\sinh\delta] & -\frac{\lambda_{ab}}{2}\exp\left(-\frac{\lambda_a}{2}\right)\sinh\delta & -\frac{\lambda_{ac}}{2}\exp\left(-\frac{\lambda_a}{2}\right)\sinh\delta \\ -\frac{\lambda_{ba}}{2}\exp\left(-\frac{\lambda_a}{2}\right)\sinh\delta & \frac{|\lambda_{ab}|^2}{\delta}\left[\frac{\exp(E^-)}{\lambda_a+2\delta} - \frac{\exp(E^+)}{\lambda_a-2\delta} + \frac{|\lambda_{ac}|^2}{|\lambda_{ab}|^2+|\lambda_{ac}|^2}\right] & -\frac{\lambda_{ba}\lambda_{ac}}{|\lambda_{ab}|^2+|\lambda_{ac}|^2}\left[1 - \frac{(\lambda_a+2\delta)\exp(E^+)}{4\delta} + \frac{(\lambda_a-2\delta)\exp(E^-)}{4\delta}\right] \\ -\frac{\lambda_{ca}}{2}\exp\left(-\frac{\lambda_a}{2}\right)\sinh\delta & -\lambda_{ca}\lambda_{ab}\left[1 - \frac{(\lambda_a+2\delta)\exp(E^+)}{4\delta} + \frac{(\lambda_a-2\delta)\exp(E^-)}{4\delta}\right] & \frac{|\lambda_{ac}|^2}{\delta}\left[\frac{\exp(E^-)}{\lambda_a+2\delta} - \frac{\exp(E^+)}{\lambda_a-2\delta}\right] + \frac{|\lambda_{ab}|^2}{|\lambda_{ab}|^2+|\lambda_{ac}|^2} \end{pmatrix}. \tag{22}$$

As in the previous example, knowledge of the coherences influences the diagonal terms, and we see that the deviation from equipartition is proportional to the relative importance of the coherent terms, as manifested in their conjugated Lagrange multipliers. An interesting feature of this matrix, however, is the result that two coherences are seen to induce a third one, which is also proportional to the Lagrange multipliers of the first two. This example shows how constraints (information) about one row and/or column of the density matrix influence other diagonal and nondiagonal elements. If the first n coherences are given in the first row, the process of maximal entropy produces an ensemble density matrix with $(n+1)^2-(n+1)-2n=n(n-1)$ additional coherent terms.

In the final example we consider a system with constraints consisting of *both* specified averages and specified elements of the density matrix. Suppose that we know the average value of some observable, typically the energy or magnetization, *and* the value of a coherence set up at $t=0$. The most probable density matrix maximizes $-\mathrm{Tr}\rho\ln\rho$, subject to the constraints

$$\begin{aligned}&\mathrm{Tr}\rho=1\ ,\\&\mathrm{Tr}\rho H=E\ ,\\&\mathrm{Tr}\rho|a\rangle\langle b|=\rho_{ba}\ ,\\&\mathrm{Tr}\rho|b\rangle\langle a|=\rho_{ab}\ ,\end{aligned}\tag{23}$$

where H is the Hamiltonian of the system and we choose the energy and ρ_{ab} as constraints. The density matrix now takes the form

$$\rho=\exp[-\lambda_0-\beta H-\lambda_{ab}|a\rangle\langle b|-\lambda_{ba}|b\rangle\langle a|]\ .\tag{24}$$

Again we make use of the Dyson equation to solve for the matrix elements of $G(E)$. The results are

$$G_{aa}=\frac{E+i\beta\epsilon}{(E+i\gamma)(E-i\gamma)}\ ,\tag{25a}$$

$$G_{bb}=\frac{E-i\beta\epsilon}{(E+i\gamma)(E-i\gamma)}\ ,\tag{25b}$$

$$G_{ab}=\frac{-i\lambda_{ab}}{(E+i\gamma)(E-i\gamma)}\ ,\tag{25c}$$

$$G_{ba}=\frac{-i\lambda_{ba}}{(E+i\gamma)(E-i\gamma)}\ ,\tag{25d}$$

$$G_{cc}=\frac{1}{E+i\beta E_c}\ ,\tag{25e}$$

$$G_{ca}=G_{cb}=G_{ac}=G_{bc}=0\ ,\tag{25f}$$

where $-\epsilon$, ϵ, E_c denote the energies of the $|a\rangle$, $|b\rangle$, and $|c\rangle$ states, respectively, and

$$\gamma=\sqrt{\lambda_{ab}^2+\beta^2\epsilon^2}\ .\tag{26}$$

Performing the Laplace transform we finally obtain

$$\rho=e^{-\lambda_0}\begin{pmatrix}\cosh\gamma+\frac{\beta\epsilon}{\gamma}\sinh\gamma & -\frac{\lambda_{ab}}{\gamma}\sinh\gamma & 0\\ -\frac{\lambda_{ba}}{\gamma}\sinh\gamma & \cosh\gamma-\frac{\beta\epsilon}{\gamma}\sinh\gamma & 0\\ 0 & 0 & \exp(-\beta E_c)\end{pmatrix}.\tag{27}$$

Once again we see that in the absence of coherences ($\lambda_{ab}\rightarrow 0$) the matrix assumes its canonical form. The coherences, however, change the diagonal terms from their canonical values. From (27) we see that off-diagonal terms of a reasonable magnitude can induce considerable change in the diagonal elements. As an example let us take $E_c-E_b=E_b-E_a=2\epsilon$, $\beta\epsilon=0.8$, $\rho_{ab}=0.2$. ρ_{bb} is changed by a factor of two from its canonical value with the same β.

III. DISCUSSION

We have shown how to construct ensemble density matrices for systems in which the imposed constraints include specification of off-diagonal (coherent) terms of the density matrix. The specification of diagonal elements provides no restriction on other elements (apart from normalization, which is trivial), whereas the specification of coherent terms influences other terms of the density matrix, both diagonal and off diagonal.

The procedures described in this paper may be applied to a variety of experiments. In standard pulsed NMR techniques,[6] one prepares some well characterized coherence and then follows the evolution in time of the system. The analysis presented here may be used for the construction of the initial density matrix.

An interesting "two-level" experiment was recently performed by Kukolich and co-workers[7] in the microwave region. A molecular beam of NH_3 was prepared in a coherent state with an ammonia maser. The beam was then scattered from various gases and scattering cross sections, as well as the decay of the initial coherence, were then measured. The interpretation of such experiments,[7,8] if done on a system with more than two levels, requires the construction of initial density matrices as discussed here.

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APPENDIX A: THE MAXIMIZATION OF THE ENTROPY SUBJECT TO NONCOMMUTING CONSTRAINTS

In this derivation we follow the discussion given by Katz.[3] Suppose we are given the expectation values of some operators (possibly noncommuting) of a system

$$\langle F_i\rangle=\mathrm{Tr}\rho F_i\qquad i=1,2,\ldots,N\ .\tag{A1}$$

We wish to find the density matrix, ρ, which maximizes the entropy (the units are chosen so that Boltzmann's constant $k=1$)

$$S=-\mathrm{Tr}\rho\ln\rho\tag{A2}$$

subject to the N constraints (A1) and the normalization condition

$$\mathrm{Tr}\rho=1\ .\tag{A3}$$

For this purpose we define the functional

$$\mathcal{L}=-\mathrm{Tr}\left\{\rho\left[\ln\rho-(\lambda_0+1)+\sum_{i=1}^{N}\lambda_iF_i\right]\right\}\ ,\tag{A4}$$

where $\lambda_0,\ldots,\lambda_N$ are Lagrange multipliers. Now we search for the unconstrained extremum of $\mathcal{L}$ with respect to variations in ρ. Let us choose a diagonal representation of ρ

$$\rho=\sum_\alpha|\alpha\rangle\rho_\alpha\langle\alpha|\ .\tag{A5}$$

The variation of ρ includes variations in $\{|\alpha\rangle\}$ and in ρ_α. Consider first variations in $\{|\alpha\rangle\}$. Define an infinitesimal transformation of the basis set $\{|\alpha\rangle\}$

$$\delta\rho=\frac{i}{\hbar}[A,\rho]\delta\theta\ ,\tag{A6}$$

where A is an arbitrary matrix and $\delta\theta$ an infinitesimal variation of a parameter. We then have

$$\delta\mathcal{L} = -\frac{i}{\hbar}\left\{\mathrm{Tr}[A, \rho]\sum_{i=1}^{N} \lambda_i F_i\right\}\delta\theta \ , \tag{A7}$$

which rearranges to

$$\delta\mathcal{L} = -\frac{i}{\hbar}\,\mathrm{Tr}\left\{A\left[\rho, \sum_{i=1}^{N} \lambda_i F_i\right]\right\}\delta\theta \ . \tag{A8}$$

The variation $\delta\mathcal{L}$ should vanish for any A.

Choosing

$$A = \frac{i}{\hbar}\left[\rho, \sum_{i=1}^{N} \lambda_i F_i\right] \ , \tag{A9}$$

we get

$$\delta\mathcal{L} = -\mathrm{Tr}\left\{\frac{i}{\hbar}\left[\rho, \sum_{i=1}^{N} \lambda_i F_i\right]\right\}^2 \delta\theta = 0 \ . \tag{A10}$$

Since the operator in the brackets is Hermitian, the trace of its square vanishes only when the operator itself vanishes. Thus,

$$\left[\rho, \sum_{i=1}^{N} \lambda_i F_i\right] = 0 \ . \tag{A11}$$

We see that ρ and $\sum_{i=1}^{N}\lambda_i F_i$ may be diagonalized simultaneously. Writing

$$\sum_{i=1}^{N} \lambda_i F_i = \sum_{|\alpha\rangle} |\alpha\rangle F_\alpha \langle\alpha| \ , \tag{A12}$$

we can represent $\mathcal{L}$ as

$$\mathcal{L} = -\sum_{\alpha} \rho_\alpha\{\ln\rho_\alpha - (\lambda_0 + 1) + F_\alpha\} \ . \tag{A13}$$

Now we impose the stationarity of $\mathcal{L}$ with respect to variations in ρ_α:

$$\delta\mathcal{L}/\delta\rho_\alpha = -[\ln\rho_\alpha - \lambda_0 + F_\alpha] = 0 \ , \tag{A14}$$

where from

$$\rho_\alpha = \exp[\lambda_0 - F_\alpha] \tag{A15}$$

and using (A5) we have

$$\rho = \sum_{|\alpha\rangle} |\alpha\rangle \exp[\lambda_0 - F_\alpha]\langle\alpha| = \exp\left[\lambda_0 - \sum_{i=1}^{N} \lambda_i F_i\right] \ . \tag{A16}$$

We reiterate that the operators F_i need not commute.

APPENDIX B: EVALUATION OF THE DENSITY MATRIX ELEMENTS

We wish to evaluate the matrix elements of

$$\rho = \exp(A) \ , \tag{B1}$$

where A is a known operator. For this we make use of the representation[10]

$$\theta(t)\exp(-iAt) = -\frac{1}{2\pi i}\int_{\xi} dE \exp(-iEt)G(E) \ , \tag{B2}$$

where

$$G(E) = (E - A + i\eta)^{-1} \tag{B3}$$

is the Laplace transform of $\exp(-iAt)$, and $\theta(t)$ is the Heavyside stepfunction. The contour ξ lies in the complex E plane, parallel to the real axis and above all the poles of $G(E)$. Thus, instead of evaluating the matrix elements $[\exp(-iAt)]_{\alpha,\beta}$, we can evaluate the corresponding elements of G, $G_{\alpha\beta}$, and perform the integration.

Evaluation of the matrix elements of G is achieved by making use of the Dyson equation[10]

$$G = G_0 + G_0 A' G \ , \tag{B4}$$

where A has been arbitrarily partitioned as

$$A = A_0 + A' \tag{B5}$$

and

$$G_0(E) = (E - A_0 + i\eta)^{-1} \ . \tag{B6}$$

In practice it is convenient to choose A_0 to be the diagonal part of A and A' the rest. Writing explicitly the matrix elements of Eq. (B4) results in N sets of N algebraic equations for each row (column) of G, where N is the size of the A matrix.[11]

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