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Generalized Master Equation for Quantum-Mechanical Systems to all Orders in the Density

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An exact generalized master equation is derived for a large quantum-mechanical system in the form of a power series in the density. This derivation is a quantum-mechanical generalization of a previous work by the author for classical systems. The quantum equation can be viewed as a time-dependent analog of the virial expansion of the quantum-mechanical partition function—for both degenerate systems (Bose-Einstein or Fermi-Dirac statistics) and nondegenerate systems. The coefficients of the series, in the quantum master equation, are explicitly given in terms of operators (Green functions) which are determined by the dynamics of isolated groups of particles and are convergent functions of the interaction potential. Equations are obtained for the off-diagonal elements of the density matrix as well as for the diagonal elements. The equation for the diagonal elements is shown to reduce to a Markoffian master equation for asymptotically long times, and an explicit expression is obtained for the "scattering" operator of this asymptotic equation.

I. INTRODUCTION

IN a recent article[1] (hereafter referred to as I) an exact generalized master equation for a classical system was derived in the form of a density expansion each term of which is a convergent function of the interaction potential.

It is the purpose of the present article to extend that result to quantum-mechanical systems. That is, to derive an exact expression for the evolution of the density matrix in the form of an expansion in powers of the density. The corresponding quantum-mechanical master equations of Van Hove, Zwanzig, and Resibois and Prigogine,[2] on the other hand, are expressed as expansions in powers of the interaction potential and are not directly applicable to singular potentials[3] nor pertinent to a given order in the density.

To accomplish our purpose the Von Neumann equation for the density matrix is cast in the form of Liouville's equation, and the resulting Von Neumann Liouville equation is treated in the same formal way as was the classical Liouville equation in I.[4]

[The Von Neumann-Liouville (VNL) formalism has been used in statistical mechanics by many authors in recent years; for example, Prigogine and Ono,[5] Zwanzig, and Resibois.[2] In Van Hove's work, however, this formalism is not taken advantage of and is complicated by the coupling between products of resolvents which arise from commutators. Ono, Prigogine, and Resibois avoid commutator complications by the clever device of introducing a new "Hamiltonian" in a representation such that the commutator in the Von Neumann equation is replaced by a "displacement" operator. In the present article we shall avoid commutator complications without introducing a new "Hamiltonian" by taking full advantage of the strict analogy between the Von Neumann equation and the classical Liouville equation.]

In Sec. II we define quantum mechanical Liouville operators in terms of which the Von Neumann equation

[1] J. Weinstock, Phys. Rev. **132**, 454 (1963). Also referred to as I.
[2] L. Van Hove, Physica **23**, 441 (1957); R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960); I. Prigogine and P. Resibois, Physica **27**, 629 (1961); P. Resibois, Physica **29**, 721 (1963).
[3] R. J. Swenson, J. Math. Phys. **4**, 544 (1963). Here, the Van Hove master equation is reformulated in terms of a convergent two-body scattering matrix.
[4] Here, however, the derivation is performed in the resolvent formalism (E plane) whereas in I it was performed explicitly in the time. The two methods are completely equivalent since they are related to each other by a Laplace transform. The reason for switching from the time plane of I to the present E plane is to demonstrate this equivalence at every stage of the derivation.
[5] I. Prigogine and S. Ono, Physica **25**, 171 (1959).

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can be viewed as Liouville's equation (VNL equation). In Sec. III we obtain the t-matrix expansion (binary collision expansion) of the formal resolvent solution of the VNL equation (this expansion is a sum of products of two-body t-matrix operators which is analogous to the Mayer f_{ij} expansion of the partition function). In Secs. IV and V there are defined *cluster* products and *irreducible cluster* products of t matrices which are identical to the Laplace transforms of their classical counterparts in I when the classical Liouville operators are replaced by quantum ones. In Sec. VI the expansion of the resolvent is regrouped in terms of irreducible clusters to obtain a generalized master equation for a *nondegenerate* quantum system which is given explicitly to all orders of the density, and is exact for all time in the limit of an infinite system. This equation, as in the classical case, can be viewed as a time-dependent analog of the equilibrium virial expansion in which the irreducible cluster of $(s+1)$ particles plays the role of the $(s+1)$th virial coefficient. A generalized master equation for a *degenerate* (Bose-Einstein or Fermi-Dirac statistics) quantum system is derived in Sec. VII. This equation involves a double sum in powers of the density due to the degeneracy statistics. There is also obtained an equation for the off-diagonal part of the density matrix—as well as for the diagonal part. Finally, in Sec. VIII it is shown that the generalized master equation approaches a Markoffian equation in the asymptotic limit of long time, and an explicit expression is derived for the scattering operator of this equation.

The results of these sections are limited to density matrices which are initially diagonal (in momentum representation this means independent of particle configurations).

II. VON NEUMANN-LIOUVILLE EQUATION

We wish to study the temporal evolution of the density matrix of a quantum-mechanical system of N particles enclosed in a box of volume V. The Hamiltonian of the system, excluding wall forces, is given by

$$H_N \equiv H_N{}^0 + V', \tag{1}$$

$$H_N{}^0 \equiv -\frac{\hbar^2}{2m}\sum_{j=1}^{N}\frac{\partial^2}{\partial \mathbf{R}_j{}^2}, \tag{2}$$

$$V' \equiv \sum_{j<s} V_{js} \equiv \sum_{j<s} V(\mathbf{R}_{js}), \tag{3}$$

where $\mathbf{R}_j$ is the vector position of particle j, $V(\mathbf{R}_{js})$ is the interaction potential between particles j and s, and $\mathbf{R}_{js} \equiv \mathbf{R}_j - \mathbf{R}_s$. We next define the corresponding quantum mechanical Liouville operators L_N, $L_N{}^0$, L_{js} by

$$Lf \equiv (1/\hbar)[H_N, f] \equiv (1/\hbar)[H_N f - f H_N], \tag{4}$$

$$L_N{}^0 f \equiv (1/\hbar)[H_N{}^0, f], \tag{5}$$

$$L_{js} f \equiv (1/\hbar)[V_{js}, f], \tag{6}$$

$$L_N \equiv L_N{}^0 + \sum_{j<s} L_{js},$$

where f denotes any function on which the L's operate.

The Von Neumann-Liouville equation for the evolution of the density matrix $\rho(t)$ of our system can now be written as

$$\partial\rho(t)/\partial t = (-i/\hbar)[H_N, \rho] \equiv -iL_N\rho(t). \tag{7}$$

This has the formal solution

$$\rho(t) = e^{-iH_N t/\hbar}\rho(0)e^{iH_N t/\hbar} \tag{8}$$

and, hence,

$$\rho(t) = e^{-itL_N}\rho(0) \equiv G_N(t)\rho(0), \tag{9}$$

where the N-particle particle propagator (Green function) $G_N(t) \equiv e^{-itL_N}$ is the formal solution of the N-particle Heisenberg equation. [Equation (9) follows easily from Eq. (8) by means of the identity

$$(L_N)^m\rho \equiv \sum_{r=0}^{m} \frac{(-1)^r m!}{r!(m-r)!}[(H_N)^{m-r}\rho(H_N)^r].] \tag{10}$$

Equation (9), it will be noted, has the same form as the solution of the classical Liouville equation in I. For this reason we may derive an exact equation for the diagonal part (diagonal elements) of $\rho(t)$ from Eq. (9)—in the form of a density expansion—in the same way that the density expansion of the classical master equation was derived from the classical Liouville equation. In Ref. 1, however, the derivation was performed in the time t plane whereas in the present case the derivation shall be performed in the Laplace transform plane (E plane).

We shall, hence, define the Laplace transform of the propagator $G_N(t)$ by $g_N(E)$ so that

$$\begin{aligned} g_N(E) &\equiv \int_0^\infty dt e^{-tE} G_N(t), \\ &\equiv (iL_N + E)^{-1}. \end{aligned} \tag{11}$$

In terms of $g_N(E)$, Eq. (9) for the formal solution of the VNL equation becomes

$$\rho(t) = \frac{1}{2\pi i}\oint dE\left(\frac{e^{+tE}}{iL_N + E}\right)\rho(0), \tag{12}$$

where the contour of integration is the usual vertical line of infinite extent which lies anywhere to right of all singularities of the integrand in the complex E plane.

The master equation for $\rho(t)$ may be derived from (12) in a manner similar to that in Ref. 1. Thus, the propagator $(iL_N + E)^{-1}$ is expanded as a sum of products of two-body propagators and the result is regrouped in terms of irreducible clusters of groups of particles—using the same cluster concept as in Mayer's well-known equilibrium theory—to obtain a density expansion for $\rho(t)$.

III. t-MATRIX EXPANSION (BINARY COLLISION EXPANSION)

The expansion of $(iL_N+E)^{-1}$ in terms of two-body propagators is generally known as the t-matrix expansion, and is simply the Laplace transform of the binary collision expansion of Ref. 1. The t-matrix expansion involves the free-particle propagator $g_0(E)$ and the two-particle propagator $g_{js}(E)$:

$$g_0(E)\equiv(iL_N{}^0+E)^{-1}, \tag{13}$$

$$g_{js}(E)\equiv(iL_N{}^0+iL_{js}+E)^{-1}. \tag{14}$$

These propagators are special cases of the n-body propagator $g_n(E)$ which we shall define here for later use as

$$g_n(E)\equiv(iL_N{}^0+i\sum_{1\leq j<s\leq n}L_{js}+E)^{-1}. \tag{15}$$

[$g_n(E)$ is thus the formal solution of the VNL equation for a system in which particles $1, 2, \cdots, n$ are interacting with each other while the remaining $(N-n)$ particles are noninteracting: it thus involves the solution of an n-body problem.]

In terms of these propagators the t-matrix expansion of $g_N(E)$ is given by[1,6]

$$g_N(E)=g_0(E)+\sum_{n=1}\sum_{\{\alpha\}}t_{\alpha_1}t_{\alpha_2}\cdots t_{\alpha_n}g_0(E), \tag{16}$$

where the binary index α_k denotes the pair of particles $j_ks_k(j_k<s_k)$ and the t-matrix operator t_{α_k} is defined by

$$t_{\alpha_k}\equiv[g_{\alpha_k}(E)-g_0(E)]g_0(E)^{-1} \tag{17}$$

and involves the solution of a two-body problem [t_α can also be defined by the usual expression $(g_0{}^{-1}t_\alpha=-iL_\alpha-iL_\alpha g_0(g_0{}^{-1}t_\alpha)$]. The summation

$$\sum_{\{\alpha\}}$$

in (16) denotes the sum of each of the binary indices $\alpha_1, \alpha_2\cdots\alpha_n$ over all the $\frac{1}{2}N(N-1)$ possible pairs of particle indices *such that no consecutive pair are the same.* [For convenience of notation we shall not always write the argument E in $g_n(E)$ or $t_\alpha(E)$.]

IV. CLUSTERS (CONNECTED PRODUCTS) OF t-MATRIX OPERATORS

As the first step in the derivation of a master equation for $\rho(t)$ from (16) and (12) we define clusters of t's in exactly the same way as clusters of f's were defined in Ref. 1. This definition of clusters is adapted from Mayer's theory and is stated as follows:

For any products of t's,

$$t_{\alpha_1}t_{\alpha_2}\cdots t_{\alpha_n}, \tag{18}$$

which appears in Eq. (16) we imagine drawing a point in configuration space for each particle (particle index) which occurs in the product. We then imagine drawing n line segments through each of the n pairs of particles indices $\alpha_1, \alpha_2\cdots\alpha_n$ so that to each t_{α_k} in this product there corresponds a line segment connecting the pair of particles α_k. If it so happens that a group of line segments connect a group of particles together, directly or indirectly, such that a continuous line passes through each particle in this group then the t's which correspond to this connected group are said to form a connected product or cluster of t's, and the particles which are so connected by this group of line segments are said to be connected to each other in a cluster (see Footnote 7 of Ref. 1).

We may now define the operator

$$[g_n(\neq i_1i_2\cdots i_{s+1};E)-g_0(E)]g_0(E)^{-1} \tag{19}$$

to be the sum of all permissible t products that can be formed from a set of n particle indices such that no pair of particle indices from among the subset $i_1, i_2\cdots i_{s+1}$ are connected to each other in a cluster. [$g_n(\neq i_1\cdots i_{s+1};E)$ is simply the Laplace transform of the propagator $G_n(\neq i_1\cdots i_{s+1})$ defined in I providing $L_N{}^0$ and L_{js} are defined by (5) and (6) instead of by their classical counterparts in I.]

A property of $g_n(\neq i_1\cdots i_{s+1};E)$ that will be used in the next section is

$$g_n(\neq i_1\cdots i_n;E)-g_0(E)=0, \tag{20}$$

since, by definition, $g_n(\neq i_1\cdots i_n;E)$ is the sum of all t products in which there are *no* particles connected to each other in a cluster.

V. IRREDUCIBLE CLUSTERS

We shall next use the operator $g_n(\neq i_1\cdots i_{s+1};E)$ to express $g_N(E)$ in a form from which one can readily prove $g_N(E)$ to be a linear functional of itself and, hence, lead to a master equation (Sec. IV). This expression for $g_n(E)$ also serves the dual purpose—to which we confine our attention in the present section—of defining the *irreducible clusters* of $(n+1)$ particles, $T_n(i_1\cdots i_{n+1};E)$, in terms of which the master equation shall appear.

This expression is given, for all $n>1$, by

$$g_n(E)\equiv g_0(E)+\sum_{s=1}^{n-1}\sum_{1\leq i,<\cdots<i_{s+1}\leq n}T_s(i_1\cdots i_{s+1};E)\times g_0(E)^{-1}g_n(\neq i,\cdots i_{s+1};E), \tag{21}$$

where the irreducible cluster $T_s(i_1\cdots i_{s+1};E)$ is to be determined so as to satisfy (21) for all n. *Equation (21), for all n, is thus to be viewed as a definition of T_s* $(i_1\cdots i_{s+1};E)$. [$T_s(i_1\cdots i_{s+1};E)$ is the Laplace transform of the irreducible cluster $V_s(i_1\cdots i_{s+1};t)$ defined in I in which the classical Liouville operators have been replaced by the quantum ones.]

[6] K. M. Watson, Phys. Rev. **103**, 489 (1956); A. J. F. Siegert and Ei Teramoto, *ibid.* **110**, 1232 (1958).

To facilitate the determination of T_s from (21) we substitute (20) into (21) and re-arrange to obtain

$$T_{n-1}(1,2\cdots n) \equiv g_n(E)-g_0(E)-\sum_{s=1}^{n-2}\sum_{1\leq i,<\cdots<i_{s+1}\leq n} T_s(i_1\cdots i_{s+1};E) \times g_0(E)^{-1}g_n(\neq i,\cdots i_{s+1};E). \quad (22)$$

Equation (22) can be solved recursively for all the T_n's by solving for successively increasing values of n. As examples we solve for T_1 and T_2 in Appendix A by setting n equal to 2 and then 3 in (22). It is found there that

$$T_1(12;E)\equiv g_2(E)-g_0(E) \equiv t_{12}g_0(E)$$

and

$$T_2(123;E)\equiv g_3(E)-g_0(E)-(t_{12}+t_{13}+t_{23})g_0(E) -(t_{12}t_{13}+t_{12}t_{23}+t_{13}t_{12}+t_{13}t_{23} +t_{23}t_{12}+t_{23}t_{13})g_0(E).$$

By repeating the procedure of Appendix A with n equal to 4, 5, 6, etc., the recursion relation, Eq. (22), can be solved uniquely for all T_n's. This would give T_n as a function of $g_{n+1}(E)$, $g_n(E)$, $\cdots g_0(E)$ so that T_n involves the solution of no more than an $(n+1)$ body problem. [The irreducible cluster $T_n(1_i\cdots n+1;E)$ can be viewed as the $(n+1)$-body generalization of the two-body t matrix, i.e., T_n can be viewed as an $(n+1)$-body *collision* operator. This is because T_n can be shown to vanish for *all* particle configurations in which all $(n+1)$ particles are not simultaneously correlated with each other. For example (see Appendix C), if any pair of particles from among 1, 2, $\cdots$, $n+1$ are sufficiently separated from each other than

$$T_n(1\cdots n+1;E)=0.$$

In addition, $T_n(1\cdots n+1;E)$ can be viewed as an analog of the Mayer irreducible cluster sum—Husimi function—since it can be expressed as a sum of irreducible products of pair functions, t's, and vanishes when any two of its particles are sufficiently separated.]

Equation (22) serves to generate all the T_n's and we shall hereafter consider T_n to be a known function.

VI. GENERALIZED MASTER EQUATION FOR A NONDEGENERATE QUANTUM SYSTEM (BOLTZMANN STATISTICS)

In this section we shall obtain the density expansion of the generalized master equation for a nondegenerate system (an analogous equation for degenerate systems is derived in Sec. VII). For this purpose Eq. (21), with $n=N$, is substituted into (12) to obtain

$$\rho(t)=\frac{1}{2\pi i}\oint dE[g_0(E)+\sum_{s=1}^{N-1}\sum_{i_1<\cdots<i_{s+1}} T_s(i_1\cdots i_{s+1};E) \times g_0(E)^{-1}g_N(\neq i_1\cdots i_{s+1};E)]e^{+tE}\rho(0). \quad (23)$$

The master equation is a closed equation for the diagonal part of $\rho(t)$, and can be derived from (23) in, essentially, two main steps. Before proceeding with this derivation, however, we shall first specify exactly what we mean by diagonal part of diagonal element.

By an element of $\rho(t)$ is meant the expectation of $\rho(t)$ between two free N-particle states (eigenfunctions of the total momentum operator). A free N-particle state $\mathbf{k}$ denotes that particles 1, 2, $\cdots$, N are in free particle states $\mathbf{k}_1$, $\mathbf{k}_2$, $\cdots$, $\mathbf{k}_N$, respectively, and is given by

$$V^{-N/2}\prod_{j=1}^{N} e^{i\mathbf{k}_j\cdot\mathbf{R}_j}\equiv V^{-N/2}e^{i\{\mathbf{k}\}\cdot\{\mathbf{R}\}}. \quad (24)$$

The symbol $\rho_{ks}(t)$, thus, denotes the following:

$$\rho_{ks}(t)\equiv V^{-N}\int d\{\mathbf{R}\}e^{-i\{\mathbf{k}\}\cdot\{\mathbf{R}\}}\rho(t)e^{i\{\mathbf{s}\}\cdot\{\mathbf{R}\}} \equiv\langle\mathbf{k}|\rho(t)|\mathbf{s}\rangle. \quad (25)$$

The diagonal part of $\rho(t)$, which will be denoted by either $D\rho(t)$ or $\rho_D(t)$, is thus defined by

$$\rho_D(t)\equiv D\rho(t)\equiv\sum_{k}|\mathbf{k}\rangle\rho_{kk}(t)\langle\mathbf{k}|. \quad (26)$$

The diagonal part of Eq. (23) can now be written as

$$\rho_D(t)=D\frac{1}{2\pi i}\oint dE[g_0(E)+\sum_{s=1}^{N-1}\sum_{i_1<\cdots<i_{s+1}} T_s(i_1\cdots i_{s+1}) \times g_0(E)^{-1}g_N(\neq i_1\cdots i_{s+1})]e^{+tE}\rho(0). \quad (27)$$

The master equation for $\rho_D(t)$ can be derived from (27) in essentially two steps. They are:

Step (1): If $\rho(0)$ is independent of the positions of the particles (this means that $\rho(0)$ is diagonal in momentum representation) then

$$DT_s(i_1\cdots i_{s+1})g_0^{-1}g_N(\neq i_1\cdots i_{s+1})\rho(0) =DT_s(i_1\cdots i_{s+1})g_0^{-1}Dg_N(\neq i_1\cdots i_{s+1})\rho(0). \quad (28)$$

Step (2): If the volume of the system is sufficiently large then

$$Dg_N(\neq i_1\cdots i_{s+1})\rho(0)=Dg_N(E)\rho(0)+O(s/V) \equiv\int_0^\infty dte^{-tE}\rho_D(t)+O(s/V). \quad (29)$$

The proofs of Eqs. (28) and (29) are given in Appendices B and C. [Equations (28) and (29), and their proofs, are analogous to their classical counterparts in I. The essential difference is that the quantum case involves the diagonal part, D, of operators whereas the classical case involves the average of these operators over configuration space.]

To obtain the desired equation for $\rho_D(t)$ we substitute

Eqs. (28) and (29) into (27) and thus find

$$\rho_D(t)=\frac{1}{2\pi i}\oint dE[Dg_0(E)+\sum_{s=1}^{N-1}\sum_{i_1<\cdots<i_{s+1}} DT_s(i_1\cdots i_{s+1}) \times g_0^{-1}\{Dg_N(E)+O(s/V)\}]e^{+tE}\rho(0). \quad (30)$$

We shall avail ourselves of the notation of equilibrium statistical mechanics and denote the diagonal part of the irreducible cluster sum by $\beta_s(E)$,

$$\beta_s(E)\equiv D\sum_{1\le i_1<\cdots<i_{s+1}\le N} T_s(i_1\cdots i_{s+1};E), \quad (31)$$

so that Eq. (30) can be written as

$$\rho_D(t)=\frac{1}{2\pi i}\oint dE\, e^{+tE}[Dg_0(E)\rho(0) +\sum_{s=1}^{N-1}\beta_s g_0^{-1}\{Dg_N+O(s/V)\}\rho(0)]. \quad (32)$$

In the asymptotic limit of infinite N and V (at constant N/V)—and within the radius of convergence of $\sum_{s=1}^{\infty}\beta_s g_0^{-1}s$—Eq. (32) becomes

$$\rho_D(t)=\frac{1}{2\pi i}\oint dE\, e^{+tE}[Dg_0+\sum_{s=1}^{\infty}\beta_s g_0^{-1}Dg_N]\rho(0). \quad (33)$$

The inverse Laplace transform on the right side of (33) may be performed by means of the convolution theorem. The inverse transform of $\beta_s(E)$ is to be denoted by the *time-dependent* irreducible cluster operator $\beta_s(t)$, i.e.,

$$\beta_s(E)\equiv\int_0^{\infty}dt\, e^{-Et}\beta_s(t)\equiv D\int_0^{\infty}dt\, e^{-Et}T_s(t). \quad (34)$$

The inversion of the integrand in (33) is simplified by the easily verified fact that if DA is the diagonal part of any operator A then, since H_0 is also diagonal,

$$L_0DA\equiv H_0DA-(DA)H_0=0. \quad (35)$$

From (35) it follows, since $\rho(0)=\rho_D(0)$, that

$$\begin{aligned} g_0(E)\rho(0)&=E^{-1}\rho(0),\\ g_0(E)^{-1}DG_N(E)&=EDG_N(E). \end{aligned} \quad (36)$$

Substituting (36) into (33) and making use of (12) as well as of the relation

$$\beta_s(t)_{t=0}=\beta_s'(t)_{t=0}=0 \quad (37)$$

[the proof of (37) is the same as that in Appendix D of Ref. 1] we find, by means of the convolution theorem, that

$$\rho_D(t)=\rho_D(0)+\int_0^t dy[\sum_{s=1}^{\infty}\beta_s'(t-y)]\rho_D(y) \quad (38)$$

which is an exact equation for $\rho_D(t)$ in the form of a density expansion. It is exact in the limit of an infinite system providing: (1) $\rho(0)$ is diagonal and (2) the scattering cross sections are finite.

The generalized master equation is obtained from (38) by simply differentiating it with respect to t and substituting (37)

$$\frac{\partial\rho_D(t)}{\partial t}=\int_0^t dy[\sum_{s=1}^{\infty}\beta_s''(t-y)]\rho_D(y). \quad (39)$$

Equation (39) is a form of the generalized master equation given explicitly to all orders of the density. It is exact for all t in the limit of an infinite "homogeneous" system.

The time-dependent cluster function $\beta_s(t)$ involves the solution of a well-defined quantum-mechanical $(s+1)$-body problem, and converges for all potentials of a finite range [$\beta_s(t)$ is determined by the solution of the Heisenberg equation for a system of $(s+1)$ isolated particles]. The cluster $T_s(t)$, of which $\beta_s(t)$ is simply the diagonal part, is the same as the classical $V_s(t)$ when the quantum Liouville operators are replaced by classical ones.

Equation (39) is equivalent to the Resibois-Prigogine master equation, as given in Ref. 2, Eq. (2.9), in the representation of *unsymmetrized* plane-wave states. The latter is expressed as an expansion in powers of the interaction potential whereas the former is expressed as an expansion in the density.

VII. DEGENERATE QUANTUM SYSTEM (BOSE-EINSTEIN OR FERMI-DIRAC STATISTICS)

In this section we shall derive a generalized master equation for a quantum degenerate system from Eq. (23). This means we must consider expectation values of the density matrix between properly symmetrized plane wave states.

If we let $\mathbf{n}$ denote such a properly symmetrized plane-wave state [for either Bose-Einstein (B.E.) or Fermi-Dirac (F.D.) statistics] then the expectation value of the density matrix operator between two such states ($\mathbf{n}$ and $\mathbf{n}'$) is denoted by

$$\rho_{nn'}(t)\equiv\langle\mathbf{n}|\rho(t)|\mathbf{n}'\rangle \quad (40)$$

and the diagonal part of $\rho(t)$ in this representation is denoted by

$$\rho_D(t)\equiv D\rho(t)\equiv\sum_n|\mathbf{n}\rangle\rho_{nn}(t)\langle\mathbf{n}|. \quad (41)$$

The derivation of a closed equation for $\rho_D(t)$ from Eq. (23), or Eq. (27), is more complicated for a degenerate system than it was in the preceding section for a nondegenerate system. The reason is simply because step (1) [Eq. (28)] does not hold in the representation of symmetrized states.

For an arbitrary representation Eq. (28) must be replaced by the identity

$$\begin{aligned} &DT_s(i_1\cdots i_{s+1})g_0^{-1}g_N(\neq i_1\cdots i_{s+1})\rho(0)\\ &\quad=DT_s(i_1\cdots i_{s+1})g_0^{-1}Dg_N(\neq i_1\cdots i_{s+1})\rho(0)\\ &\quad\quad+DT_s(i_1\cdots i_{s+1})g_0^{-1}\mathbf{O}_Dg_N(\neq i_1\cdots i_{s+1})\rho(0), \end{aligned} \quad (42)$$

where the operator $\mathbf{O}_D$ denotes the *off-diagonal* part of the operators to its right

$$\mathbf{O}_D g_N\rho(0)\equiv g_N\rho(0)-Dg_N\rho(0).$$

[In the representation of unsymmetrized eigenfunctions the last term on the right of (42) vanishes exactly (as shown in Appendix C) and Eq. (42) then reduces to Eq. (28).]

To obtain the master equation for $\rho_D(t)$ (in any representation) we first substitute Eqs. (42) and (29) into the diagonal part of Eq. (23) and then follow the same steps as from Eq. (30) to Eq. (38) for the first term on the right side of (42) [Eq. (29) holds in any representation]. We thus find that

$$\rho_D(t)=\rho_D(0)+\int_0^t dy[\sum_{s=1}^{\infty}\beta_s'(t-y)]\rho_D(y)$$
$$+D\oint dE\sum_{s=1}^{\infty}\sum_{i_1<\cdots<i_{s+1}}T_s(i_1\cdots i_{s+1})$$
$$\times g_0^{-1}\mathbf{O}_D g_N(\neq i_1\cdots i_{s+1})e^{+tE}\rho(0), \quad (43)$$

where $\beta_s(t)$ is defined as the diagonal part of $T_s(t)$ in the new representation:

$$\beta_s(t)\equiv DT_s(t).$$

The off-diagonal operator $\mathbf{O}_D g_N$ can be expressed in terms of Dg_N. This is done in Appendix D where it's found, in the limit of an infinite system,

$$\mathbf{O}_D g_N\rho(0)=^{\text{nmc}}\{\sum_{k=1}^{\infty}(\mathbf{O}_D T g_0^{-1})^k\}Dg_N\rho(0)$$
$$=^{\text{nmc}}\{\mathbf{O}_D T g_0^{-1}(1-\mathbf{O}_D T g_0^{-1})^{-1}\}Dg_N\rho(0) \quad (44)$$

where $T\equiv T(E)$ is defined by

$$T\equiv\sum_{s=1}^{\infty}\sum_{i_1<\cdots<i_{s+1}}T_s(i_1\cdots i_{s+1}) \quad (45)$$

and the superscript nmc (*not multiply connected*) on the brackets denotes that, in the expansion of the terms within the bracket, we retain only those ordered products of $T_s(i_1\cdots i_{s+1})$ operators which are *not multiply connected* to each other with respect to particle indices:

An ordered product of T_s's is called nmc if the term which appears to the right of any T_s, say $T_s(l_1\cdots l_{s+1})$, in that product does not have any pair of particles from among $l_1, \cdots, l_{s+1}$ connected to each other in a cluster.[7] [For example, the product

$$T_1(l_1l_2)g_0^{-1}T_3(l_3l_4l_5l_6)g_0^{-1}T_2(l_7l_8l_9)g_0^{-1}\cdots$$

is nmc if: the term to right of $T_1(l_1l_2)$ does not have l_1 and l_2 connected to each other in a cluster, the term to the right of $T_3(l_3l_4l_5l_6)$ does not have any pair of particles from among l_3, l_4, l_5, and l_6 connected to each other in a cluster, and so on.]

Equation (44) is next substituted into the sum on the right side of (43), and use is made of (29) followed by (45) and (37) to obtain

$$\sum_s\sum_{i_1<\cdots<i_{s+1}}T_s(i_1\cdots i_{s+1})g_0^{-1}\mathbf{O}_D g_N(\neq i_1\cdots i_{s+1})\rho(0)$$
$$=\sum_s\sum_{i_1<\cdots<i_{s+1}}T_s(i_1\cdots i_{s+1})g_0^{-1}\,^{\text{nmc}}\{\mathbf{O}_D T g_0^{-1}(1-\mathbf{O}_D T g_0^{-1})^{-1}\}_{(\neq i\ldots i_{s+1})}Dg_N(\neq i_1\cdots i_{s+1})\rho(0)$$
$$=^{\text{nmc}}\{Tg_0^{-1}\mathbf{O}_D T g_0^{-1}(1-\mathbf{O}_D T g_0^{-1})^{-1}\}Dg_N\rho(0)$$
$$=^{\text{nmc}}\{Tg_0^{-1}(1-\mathbf{O}_D T g_0^{-1})^{-1}\mathbf{O}_D T\}EDg_N\rho(0). \quad (46)$$

[The subscript $(\neq i_1\cdots i_{s+1})$ on the bracket denotes that no term in the expansion of the bracket is to have any pair of particles from among $i_1\cdots i_{s+1}$ connected to each other in a cluster.]

Defining an operator $K(t)$, and its transform $K(E)$, by

$$K(E)\equiv\int_0^{\infty}dte^{-tE}K(t)$$
$$\equiv D(^{\text{nmc}}\{Tg_0^{-1}(1-\mathbf{O}_D T g_0^{-1})^{-1}\mathbf{O}_D T\}) \quad (47)$$

and substituting (46) into (43) there results the closed equation

$$\rho_D(t)=\rho_D(0)+\int_0^t dy[K'(t-y)+\sum_{s=1}^{\infty}\beta_s'(t-y)]\rho_D(y). \quad (48)$$

Differentiating (48) with respect to t and making use of (37) we finally obtain

$$\frac{\partial\rho_D(t)}{\partial t}=\int_0^t dy[K''(t-y)+\sum_{s=1}^{\infty}\beta_s''(t-y)]\rho_D(y). \quad (49)$$

This is a generalized master equation for a quantum degenerate system, and it is exact in the limit of an infinite "homogeneous" system. Although we have specified that diagonal parts, and expectation values, of operators are in the representation of symmetrized single-particle states (B.E. or F.D. statistics) Eq. (49) actually holds in any representation for which $\rho(0)=\rho_D(0)$. In a representation of unsymmetrized single-

[7] We use the notion of connectivity in the same sense as in equilibrium cluster theory except that here the clusters $T_s(i_1\cdots i_{s+1})$ are noncommutative so that ordering is important.

particle states $K''(t-y)$ vanishes exactly and (49) reduces to (39).

VIII. LONG TIME LIMIT—MARKOFFIAN EQUATION

It has been shown (see Sec. III of Ref. 1) that the classical generalized master equation reduces to a Markoffian equation in the asymptotic limit of long time. This was a consequence of the fact that the kernel of the former equation rapidly vanishes with time. Since the kernel, $[K''(t)+\sum_{s=1}^{\infty}\beta_s''(t)]$, of the quantum generalized master equation also rapidly vanishes with time (although we do not prove it here) we may use the same analysis as in Ref. 1 to prove that Eq. (49) asymptotically reduces to a Markoffian equation. We, thus, find that

$$\partial\rho_D(t)/\partial t=\Lambda(E^*)\rho_D(t) \quad (\text{large } t), \tag{50}$$

where the Markoffian scattering operator $\Lambda(E)$ is defined by

$$\Lambda(E)\equiv\int_0^{\infty} dt e^{-tE}[K''(t)+\sum_{s=1}^{\infty}\beta_s''(t)] \tag{51}$$

and E^* is defined as the solution (real) of

$$[E-\Lambda(E)]\rho_D(0)=0. \tag{52}$$

Equation (52) is an implicit definition of $\Lambda(E^*)$. An explicit expression for $\Lambda(E^*)$ can be obtained by simply "inverting" (52) (this was not done in Ref. 1) as follows; a function $\omega(E)$ is defined by

$$\omega\equiv\Lambda(E)-E. \tag{53}$$

Since $\Lambda'(0)\neq 0$ and $\Lambda(E)$ is analytic in the neighborhood of $E=0$ (see Ref. 1) it can be shown that, in this neighborhood, the inverse of (53) exists, is unique, and is given by[8]

$$E=\sum_{n=1}^{\infty} A_n[\omega-\Lambda(0)]^n, \tag{54}$$

where

$$A_n\equiv\frac{1}{n!}\left\{\frac{d^{n-1}}{dE^{n-1}}\frac{E}{[\Lambda(E)-E]^n}\right\}_{E=0}. \tag{55}$$

Since E^* is the solution of $\omega(E)=0$ we simply set $\omega=0$ in (54) to obtain

$$\Lambda(E^*)=E^*=\sum_{n=1}^{\infty}(-1)^n A_n[\Lambda(0)]^n \tag{56}$$

which is an explicit expression for $\Lambda(E^*)$ in terms of $\Lambda(0)$ and the derivatives $\Lambda^n(0)$.

APPENDIX A

The solution of the recursion relation, Eq. (22), for $T_1(12)$ and $T_2(123)$ is, formally, the same as that for its classical counterpart in I so that we can be brief. Setting n equal to two in (22) yields

$$\begin{aligned} T_1(12;E)\equiv g_2(E)-g_0(E)&\equiv(il_{12}+il_N{}^0+E)^{-1}\\ &\quad-(il_N{}^0+E)^{-1} \qquad \text{(A1)}\\ &\equiv t_{12}g_0(E)\end{aligned}$$

which only involves the solution of a two-body problem.

To obtain $T_2(123)$ we set n equal to three in (22)

$$\begin{aligned} T_2(123;E)\equiv g_3(E)-g_0(E)&\\ -\sum_{1\leq i_1<i_2\leq 3} T_1(i_1i_2;E)g_0(E)^{-1}g_3(\neq i_1i_2;E).& \qquad \text{(A2)}\end{aligned}$$

But by definition,

$$g_3(\neq 12)\equiv g_0+(t_{13}+t_{23})g_0 \tag{A3}$$

so that (A2) becomes

$$\begin{aligned} T_2(123;E)\equiv g_3-g_0-T_1(12)g_0^{-1}(1+t_{13}+t_{23})g_0&\\ -T_1(13)g_0^{-1}(1+t_{12}+t_{23})g_0&\\ -T_1(23)g_0^{-1}(1+t_{12}+t_{13})g_0.& \qquad \text{(A4)}\end{aligned}$$

Substituting (A1) into (A4), and re-arranging, we obtain

$$\begin{aligned} T_2(123;E)\equiv g_3(E)-g_0(E)-(t_{12}+t_{13}+t_{23})g_0(E)&\\ -(t_{12}t_{13}+t_{12}t_{23}+t_{13}t_{12}+t_{13}t_{23}+t_{23}t_{12}&\\ +t_{23}t_{13})g_0(E)& \qquad \text{(A5)}\end{aligned}$$

which determines $T_2(123;E)$ in terms of $g_3(E)$ [see Eq. (15)] and t, and involves the solution of only a three-body problem.

APPENDIX B

To begin the proof of Eq. (28), step (1), we note that in matrix notation $T_s(i_1\cdots i_{s+1};E)g_0(E)^{-1}$ is a four-index (tetradic) operator. This is a direct consequence of the fact that L is a commutator. For example,

$$\begin{aligned} \langle\mathbf{k}|g_{12}(E)\rho|\mathbf{r}\rangle&\equiv\langle\mathbf{k}|\int_0^{\infty}dt e^{-Et}e^{-it(L_N{}^0+L_{12})}\rho|\mathbf{r}\rangle\\ &\equiv\langle\mathbf{k}|\int_0^{\infty}dt e^{-Et}e^{-it\hbar^{-1}(H_N{}^0+V_{12})}\rho e^{it\hbar^{-1}(H_N{}^0+V_{12})}|\mathbf{r}\rangle\\ &=\sum_{m,p}\int_0^{\infty}dt e^{-Et}\{e^{-it\hbar^{-1}(H_N{}^0+V_{12})}\}_{km}\rho_{mp}\{e^{it\hbar^{-1}(H_N{}^0+V_{12})}\}_{pr}\\ &=\sum_{m,p}\{g_{12}(E)\}_{krmp}\rho_{mp}, \end{aligned} \tag{B1}$$

[8] C. Carathéodory, *Theory of Functions* (Chelsea Publishing Company, New York, 1958).

where the tetradic matrix element $g_{12}(E)_{krmp}$ is defined by

$$\{g_{12}(E)\}_{krmp}\equiv\int_0^\infty dt e^{-Et}\{g_{12}(t)\}_{krmp}$$
$$\equiv\int_0^\infty dt e^{-Et}\{e^{-it\hbar^{-1}(H_N{}^0+V_{12})}\}_{km}\times\{e^{it\hbar^{-1}(H_N{}^0+V_{12})}\}_{pr}. \quad \text{(B2)}$$

In this notation a diagonal element of the left-hand member of (28) can be written as

$$\langle\mathbf{k}|T_s(i_1\cdots i_{s+1})g_0^{-1}g_N(\neq i_1\cdots i_{s+1})\rho(0)|\mathbf{k}\rangle$$
$$=\sum_{m,p}\{T_s(i_1\cdots i_{s+1})g_0^{-1}\}_{kkmp}\times\{g_N(\neq i_1\cdots i_{s+1})\rho(0)\}_{mp}. \quad \text{(B3)}$$

But $T_s(i_1\cdots i_{s+1})g_0^{-1}$ contains iteration terms (Li_1i_2, Li_1i_3, etc.) between particles $i_1i_2\cdots i_{s+1}$ only. This is because $T_s(i_1\cdots i_{s+1})$ contains ti_1i_2, ti_1i_3, etc. (see Appendix A of Ref. 1 for further details). Consequently, $T_s(i_1\cdots i_{s+1})g_0^{-1}$ changes the relative "momenta" of only particles $i_1,\cdots,i_{s+1}$.[1] The "momenta" of the remaining $(N-s-1)$ particles cannot change. In other words, the intermediate states m and p can only differ from each other, or from the state k, in the momentum eigenvalues of particles $i_1\cdots i_{s+1}$. Hence, if $\mathbf{m}_j$ denotes the "momentum" of particle j in the N-particle state m then, for $j\neq i_1,\cdots,i_{s+1}$,

$$\mathbf{m}_j=\mathbf{p}_j=\mathbf{k}_j \quad (j\neq i_1\cdots i_{s+1}). \quad \text{(B4)}$$

The "momentum" of the center of mass of particles $i_1\cdots i_{s+1}$ is also constant; i.e.,

$$\mathbf{m}_{i_1}+\cdots+\mathbf{m}_{i_{s+1}}=\mathbf{p}_{i_1}+\mathbf{p}_{i_2}+\cdots\mathbf{p}_{i_{s+1}}. \quad \text{(B5)}$$

On the other hand, the operator $g_N(\neq i_1\cdots i_{s+1})\rho(0)$ contains no interactions, or forces, between particles $i_1,\cdots i_{s+1}$, and is, in fact, entirely independent of the relative vector positions between particles $i_1\cdots i_{s+1}$. [This follows from the fact that $g_N(\neq i_1\cdots i_{s+1})$ does not have two or more particles from among $i_1\cdots i_{s+1}$ connected to each other in a cluster, and $\rho(0)$ is independent of positions—see Appendix A of Ref. 1. The operator $g_N(\neq i_1\cdots i_{s+1})\rho(0)$ depends upon the positions of particles $i_1\cdots i_{s+1}$ in the form of momentum operators only.] This means, when combined with (B5), that the "momenta" of particles $i_1\cdots i_{s+1}$ in the state m must be equal to their "momenta" in the state p:

$$\mathbf{m}_j=\mathbf{p}_j \quad (j=i_1,i_2\cdots i_{s+1}). \quad \text{(B6)}$$

Combining (B4) with (B6) we see that, in (B3),

$$\mathbf{m}_j=\mathbf{p}_j \quad (\text{all } j)$$

and, hence,

$$m=p. \quad \text{(B7)}$$

Substituting (B7) into (B3) then yields

$$\langle\mathbf{k}|T_s(i_1\cdots i_{s+1})g_0^{-1}g_N(\neq i_1\cdots i_{s+1})\rho(0)|\mathbf{k}\rangle$$
$$=\sum_m\{T_s(i_1\cdots i_{s+1})g_0^{-1}\}_{kkmm}\{g_N(\neq i_1\cdots i_{s+1})\rho(0)\}_{mm}$$
$$=\langle\mathbf{k}|T_s(i_1\cdots i_{s+1})g_0^{-1}Dg_N(\neq i_1\cdots i_{s+1})\rho(0)|\mathbf{k}\rangle. \quad \text{(B8)}$$

Multiplying both sides of (B8) by $|\mathbf{k}\rangle\langle\mathbf{k}|$ and summing over all k finally yields the desired result

$$DT_s(i_1\cdots i_{s+1})g_0^{-1}g_N(\neq i_1\cdots i_{s+1})\rho(0)$$
$$=DT_s(i_1\cdots i_{s+1})g_0^{-1}Dg_N(\neq i_1\cdots i_{s+1})\rho(0) \quad \text{(B9)}$$

which is Eq. (28).

APPENDIX C

The proof of Eq. (29), step (2), is strictly analogous to that of its classical counterpart in I (Appendix B) so that we will be brief. We first note that if $V_\alpha(\mathbf{R}_\alpha)$ is a short-range potential then (as for f_α in I)

$$t_\alpha\equiv(g_\alpha-g_0)g_0^{-1}=-g_0L_\alpha g_\alpha g_0^{-1}, \quad \text{(C1)}$$

is zero, since L_α is proportional to V_α, unless R_α is less than some well-defined length of finite extent. This length will depend upon E [since $g_0(E)$ operates on L_α in (C1)] as well as upon the range of V_α but is *independent of the total volume V of the system.*

It then follows, as in I, that a cluster (connected product) of t_α's is zero whenever the separation between any two of the particles in the cluster is greater than some finite distance.

Hence, since $[G_N-G_N(\neq i_1\cdots i_{s+1})]$ is defined as the sum of all t products which contain two or more of the particles $i_1\cdots i_{s+1}$ connected to each other in a cluster, it follows that $G_N-G_N(\neq i_1\cdots i_{s+1})$ will be zero when particles $i_1\cdots i_{s+1}$ are all simultaneously separated from each other by more than some finite distance.

There thus exists the finite regions (independent of V)

$$V(i_1i_2),\ V(i_1i_3),\cdots,\ V(i_1i_{s+1}),$$

such that

$$G_N(E)-G_N(\neq i_1\cdots i_{s+1};E)=0 \quad \text{(C2)}$$

when $\mathbf{R}_{i_1i_2}$ lies *outside* of the region $V(i_1i_2)$, $R_{i_1i_3}$ lies *outside* of $V(i_1i_3)$, etc.

As a consequence of (C2) one can write, with $\{\mathbf{k}(s)\}\cdot\{R(s)\}\equiv(\mathbf{k}_{i_1}\cdot\mathbf{R}_{i_1}+\mathbf{k}_{i_2}\cdot\mathbf{R}_{i_2}+\cdots+\mathbf{k}_{i_{s+1}}\cdot\mathbf{R}_{i_{s+1}})$

$$V^{-(s+1)}\int_V d\mathbf{R}_{i_1}\int_{V-V(i_1i_2)}d\mathbf{R}_{i_1i_2}\cdots\int_{V-V(i_1i_{s+1})}d\mathbf{R}_{i_1i_{s+1}}e^{-i\{\mathbf{k}(s)\}\cdot\{\mathbf{R}(s)\}}[G_N-G_N(\neq i_1\cdots i_{s+1})]\rho(0)e^{i\{\mathbf{k}(s)\}\cdot\{\mathbf{R}(s)\}}=0, \quad \text{(C3)}$$

where the region of integration $V-V(i_1i_2)$ denotes that we integrate $\mathbf{R}_{i_1i_2}$ over all of the volume V except for the region $V(i_1i_2)[\int_{V-V(i_1i_2)}\equiv\int_V-\int_{V(i_1i_2)}]$.

In the limit of infinite V the ratio of the volume of $V(i_1 i_2)$ to the volume V approaches zero so that we can obtain the following from (C3), see I for details:

$$V^{-(s+1)}\int_V d\mathbf{R}_{i_1}\int_V d\mathbf{R}_{i_1 i_2}\cdots\int_V d\mathbf{R}_{i_1 i_{s+1}} e^{-i\{\mathbf{k}(s)\}\cdot\{\mathbf{R}(s)\}}[G_N - G_N(\neq i_1\cdots i_{s+1})]\rho(0)^{i\{\mathbf{k}(s)\}\cdot\{\mathbf{R}(s)\}} = O(s/V). \quad \text{(C4)}$$

If we let $\{\mathbf{k}(\neq s)\}$ and $\{\mathbf{R}(\neq s)\}$ denote the set of momentum eigenvalues and vector positions, respectively, of all particles except $i_1\cdots i_{s+1}$ then we can take the expectation value of (C4) between the states $\{\mathbf{k}(\neq s)\}$ to obtain

$$V^{-N}\int d\{\mathbf{R}(\neq s)\}\int d\mathbf{R}_{i_1}\int d\mathbf{R}_{i_1 i_2}\cdots\int d\mathbf{R}_{i_1 i_{s+1}} e^{-i\{\mathbf{k}(\neq s)\}\cdot\{\mathbf{R}(\neq s)\}}$$
$$\times e^{-i\{\mathbf{k}(s)\}\cdot\{\mathbf{R}(s)\}}[G_N - G_N(\neq i_1\cdots i_{s+1})]\rho(0) e^{i\{\mathbf{k}(s)\}\cdot\{\mathbf{R}(s)\}} e^{i\{\mathbf{k}(\neq s)\}\cdot\{\mathbf{R}(\neq s)\}}$$
$$\equiv \langle\mathbf{k}|[G_N - G_N(\neq i_1\cdots i_{s+1})]\rho(0)|\mathbf{k}\rangle = O(s/V). \quad \text{(C5)}$$

Multiplying both sides of (C5) by $|\mathbf{k}\rangle\langle\mathbf{k}|$ and summing over all k we obtain the desired result:

$$DG_N(E)\rho(0) - DG_N(\neq i_1\cdots i_{s+1})\rho(0) = O(s/V). \quad \text{(C6)}$$

APPENDIX D

The derivation of Eq. (44) begins with the off-diagonal part of Eq. (21) operating on $\rho(0)$. If we substitute $g_N(\neq i_1\cdots i_{s+1}) = Dg_N(\neq i_1\cdots i_{s+1}) + \mathbf{O}_D g_N(\neq i_1\cdots i_{s+1})$ and $Dg_N(\neq i_1\cdots i_{s+1}) = Dg_N + O(V^{-1})$ into the off-diagonal part of Eq. (21) we obtain

$$\mathbf{O}_D g_N(E)\rho(0) = \mathbf{O}_D\sum_{s=1}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\})g_0^{-1}Dg_N(E)\rho(0)$$
$$+\mathbf{O}_D\sum_{s=1}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\})g_0^{-1}\mathbf{O}_D g_N(\neq\{i_{s+1}\})\rho(0) + O(V^{-1}), \quad \text{(D1)}$$

where we have used $\rho(0) = \rho_D(0)$ to obtain

$$\mathbf{O}_D g_0(E)\rho(0) = \mathbf{O}_D g_0(E)\rho_D(0) = 0, \quad \text{(D2)}$$

and $\{i_{s+1}\}$ denotes the set of $s+1$ particles $i_1\cdots i_{s+1}$.

Equation (D1), together with (29), is a recursion relation for $\mathbf{O}_D g_N\rho(0)$ in terms of $Dg_N\rho(0)$.

If we subtract, from both sides of (D1), all t products which have two or more particles from among $\{j_{l+1}\}$ connected to each other in a cluster we obtain, with (29),

$$\mathbf{O}_D g_N(\neq\{j_{l+1}\}) = \mathbf{O}_D\sum_s\sum_{i_1<\cdots<i_{s+1}\neq\{j_{l+1}\}} T_s(\{i_{s+1}\})g_0^{-1}Dg_N\rho(0)$$
$$+\mathbf{O}_D\sum_s\sum_{i_1<\cdots<i_{s+1}\neq\{j_{l+1}\}} T_s(\{i_{s+1}\})g_0^{-1}\mathbf{O}_D g_N(\neq\{i_{s+1}\})\rho(0), \quad \text{(D3)}$$

where the subscript $\neq\{j_{l+1}\}$ on the sum means that we exclude, from this sum, those values of $i_1, i_2\cdots i_{s+1}$ for which $T_s(\{i_{s+1}\})g_0^{-1}g_N(\neq\{i_{s+1}\})$ contains two or more particles from among $\{j_{l+1}\}$ connected to each other in a cluster.

Substituting (D3) into the last term on the right of (D1) we have

$$\mathbf{O}_D g_N(E)\rho(0) = \mathbf{O}_D T g_0^{-1}Dg_N\rho(0) + {}^{\text{nmc}}\{(\mathbf{O}_D T g_0^{-1})^2\}Dg_N\rho(0) + {}^{\text{nmc}}\{(\mathbf{O}_D T g_0^{-1})^2\mathbf{O}_D g_N\rho(0)\} + O(V^{-1}), \quad \text{(D4)}$$

where

$$T \equiv \sum_{s=1}^{\infty}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\}) \quad \text{(D5)}$$

and the superscript nmc (*not multiply connected*) on a bracket denotes that, of all the ordered products of $T_s(\{i_{s+1}\})$ operators which appear in the expansion of the term within a bracket, we retain only those which are *not multiply connected* to each other with respect to particle indices. By an nmc product of operators we mean the following:

An ordered product of T_s's is called nmc if the term which appears to the right of any T_s, say $T_s(\{j_{s+1}\})$, in that product does not have two or more particles from among $\{j_{s+1}\}$ connected to each other in a cluster.

For example,

$$(1)\quad {}^{\mathrm{nmc}}\{T^2\}\equiv {}^{\mathrm{nmc}}\{\sum_{s=1}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\})\sum_{l=1}\sum_{j_1<\cdots<j_{l+1}} T_l(\{j_{l+1}\})\}$$

$$\equiv\sum_{s=1}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\})\sum_{l=1}\sum_{j_1<\cdots<j_{l+1}\neq\{i_{s+1}\}} T_l(\{j_{l+1}\}). \quad \text{(D6)}$$

$$(2)\quad {}^{\mathrm{nmc}}\{(\mathbf{O}_D T g_0^{-1})^2\mathbf{O}_D g_N\rho(0)\}\equiv \mathbf{O}_D\sum_{s=1}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\})g_0^{-1}$$

$$\times\mathbf{O}_D\sum_{l=1}\sum_{j_1<\cdots<j_{l+1}\neq\{i_{s+1}\}} T_l(\{j_{l+1}\})g_0^{-1}\mathbf{O}_D g_N(\neq\{j_{l+1}\})\rho(0). \quad \text{(D7)}$$

$$(3)\quad {}^{\mathrm{nmc}}\{T\}\equiv T.$$

To continue the derivation of Eq. (44) we substitute (D3) into the third term on the right of (D4) to obtain

$$\mathbf{O}_D g_N(E)\rho(0)={}^{\mathrm{nmc}}\{(\mathbf{O}_D T g_0^{-1})+(\mathbf{O}_D T g_0^{-1})^2+(\mathbf{O}_D T g_0^{-1})^3\}Dg_N\rho(0)+{}^{\mathrm{nmc}}\{(\mathbf{O}_D T g_0^{-1})^3\mathbf{O}_D g_N\rho(0)\}. \quad \text{(D8)}$$

By repeated substitutions of (D3) into (D8) we eventually obtain

$$\mathbf{O}_D g_N(E)\rho(0)={}^{\mathrm{nmc}}\{(\mathbf{O}_D T g_0^{-1})+(\mathbf{O}_D T g_0^{-1})^2+\cdots\}Dg_N\rho(0)+O(V^{-1}). \quad \text{(D9)}$$

[The process of repeated substitution into (D8) eventually terminates since the last term on the right side of (D8) eventually becomes

$${}^{\mathrm{nmc}}\{(\mathbf{O}_D T g_0^{-1})(\mathbf{O}_D T g_0^{-1})\cdots(\mathbf{O}_D T g_0^{-1})\mathbf{O}_D g_N\rho(0)\}$$

$$\equiv[\mathbf{O}_D\sum_{s}\sum_{i_1<\cdots<i_{s+1}} T_s(\{i_{s+1}\})g_0^{-1}][\mathbf{O}_D\sum_{k}\sum_{h_1<\cdots<h_{k+1}\neq\{i_{s+1}\}} T_k(\{h_{k+1}\})g_0^{-1}]$$

$$\cdots[\mathbf{O}_D\sum_{l}\sum_{j_1<\cdots<j_{l+1}\neq\{1,2,\cdots N\}} T_l(\{j_{l+1}\})g_0^{-1}]\mathbf{O}_D g_N(\neq\{j_l+1\})\rho_0=0.$$

That is, we eventually run out of particles.] In the limit of an infinite system (D9) approaches the desired result

$$\mathbf{O}_D g_N(E)\rho(0)={}^{\mathrm{nmc}}\{\sum_{k=1}^{\infty}(\mathbf{O}_D T g_0^{-1})^k\}Dg_N(E)\rho(0),$$

$$={}^{\mathrm{nmc}}\{\mathbf{O}_D T g_0^{-1}(1-\mathbf{O}_D T g_0^{-1})^{-1}\}Dg_N(E)\rho(0). \quad \text{(D10)}$$