Simplified Derivation of the Binary Collision Expansion and Its Connection with the Scattering Operator Expansion*

A. J. F. SIEGERT AND EI TERAMOTO
Northwestern University, Evanston, Illinois
(Received February 24, 1958)

The binary collision expansion for the density matrix of a system of N particles with pair interaction was derived by Huang, Lee, and Yang by expansion in the interaction and subsequent summation over terms represented by certain classes of diagrams. A simpler derivation has been obtained by the use of the $N(N-1)/2$ integral equations which relate the density matrix of the system to the density matrices of systems in which only one pair of particles interacts. Successive substitution of the integral equations into each other yields an expansion which by a trivial additional step becomes the binary collision expansion. Our derivation shows also that the binary collision expansion is the Laplace inverse of the coordinate representation of the expansion in terms of scattering operators.

I.

IN a paper on the many-body problem in quantum mechanics and quantum statistical mechanics,[1] Lee and Yang have presented a number of important results obtained by a "binary collision method"[2] applicable to systems whose interaction is the sum of pair potentials. This method consists essentially in the summation of certain classes of terms in the expansion of the density matrix $\exp(-H/kT)$ obtained by treating the total interaction energy of the system as a perturbation. The terms of the resulting expansion are integrals of products containing the coordinate representations of the density matrices of the one- and two-particle system and a matrix X, which is the product of a pair potential and the density matrix of the two-particle system with this pair potential. Since the interaction potential occurs only in this combination, the terms of the binary collision series are integrable even in the case of infinite repulsive potentials.

Some of the results obtained by this method have since been rederived by Lee, Huang, and Yang by a different method,[3] but the binary collision method is considered by these authors to be still of importance for the further development of the theory for the reasons stated in reference 3, p. 1142. It may, therefore, be of interest to have a more elementary and direct derivation of the binary collision expansion. This derivation is obtained, by successive substitutions, from the integral equations which connect the coordinate representation of the density matrix of a system with pair interactions with the density matrices of systems in which only one pair of particles interacts. Our derivation shows also that the binary collision expansion is the Laplace inverse of the expansion in two-body scattering operators.[4]

The integral equations used here are the usual Green's function or propagator equations, which relate the principal solutions of two Bloch equations with different potentials. They become especially transparent if the coordinate representation of the density matrix is interpreted formally as the transition probability density for the Brownian movement of a point in configuration space in the presence of absorption.[5] The integral equations then result from the simple counting arguments used in the theory of Markoff processes.[6]

II.

We consider a system of N point particles with interaction energy $V(q)$, where q denotes a point in the $3N$-dimensional configuration space. We define the function $G(q_0,t_0|q,t)$ as the principal solution of the Bloch equation

$$-\partial G/\partial t=\mathcal{H}G, \tag{1}$$

where $\mathcal{H}$ is the Hamiltonian of the system. The function G is understood to satisfy boundary conditions (e.g., vanishing on the walls of the container) or periodicity conditions, and the "initial" condition

$$G(q_0,t_0|q,t_0)=\delta(q-q_0). \tag{2}$$

Since, for the problems of interest, $\mathcal{H}$ does not depend on t, G does not depend on t and t_0 separately but only on $t-t_0$.

The partition function Q_N of the system at temperature T is determined by

$$Q_N=\int G(q,0|q,(kT)^{-1})dq, \tag{3}$$

for Boltzmann statistics, where dq is the volume element in configuration space, and by

$$Q_N=\frac{1}{N!}\int\sum_P G(q,0|Pq,(kT)^{-1})dq, \tag{4}$$

* Work supported by the National Science Foundation.
[1] T. D. Lee and C. N. Yang, Phys. Rev. **105**, 1119 (1957).
[2] This method was outlined at the International Conference on Theoretical Physics, Seattle, September 1956, and by Huang, Lee, and Yang [lecture of C. N. Yang at the Stevens Conference on the Many-Body Problem, January 1957 (to be published)].
[3] Lee, Huang, and Yang, Phys. Rev. **106**, 1135 (1957).
[4] K. Watson, Phys. Rev. **103**, 489 (1956), Eq. (27).
[5] See, for instance, A. J. F. Siegert, Phys. Rev. **86**, 621 (1952).
[6] D. A. Darling and A. J. F. Siegert, Proc. Natl. Acad. Sci. U. S. **42**, 525 (1956), and Inst. Radio Engrs. Transactions of the Professional Group on Information Theory **IT-3**, 32 (1957); pp. 33 and 34, Eqs. (7) and (8).

for Bose statistics, where Pq is the configuration point obtained from q by the permutation P of all particle numbers and the sum extends over all permutations.

It should be emphasized that even if G were known exactly, the integration required in Eq. (3), for instance, is at least as difficult to perform as the corresponding integration in the classical case if the particles have hard cores, since the integrand vanishes when two particles overlap. Individual energy levels, however, such as the ground-state energy, could be obtained without integration over all q space from $G(q_0,t_0|q,t)$ for any pair of points q_0, q, for which the eigenfunctions belonging to the desired energy level do not vanish.

If the principal solutions G and G_α of the Bloch equation with interaction energies V and V_α, respectively (and the same boundary or periodicity condition), exist, they are related by the integral equations

$$G(q_0,t_0|q,t)=G_\alpha(q_0,t_0|q,t)-\int_{t_0}^{t}dt'\int dq' G_\alpha(q_0,t_0|q't')\times[V(q')-V_\alpha(q')]G(q',t'|q,t), \quad (5)$$

and

$$G(q_0,t_0|q,t)=G_\alpha(q_0,t_0|q,t)-\int_{t_0}^{t}dt'\int dq' G(q_0,t_0|q',t')\times[V(q')-V_\alpha(q')]G_\alpha(q',t'|q,t). \quad (5a)$$

Either of these integral equations determines G uniquely.[7] Boundary, periodicity, and symmetry conditions imposed on G_α, in both q_0 and q, are therefore also satisfied by G in both q_0 and q.

It is convenient to introduce an abbreviated notation for a type of integral which occurs frequently in the following calculations. We define the symbol $\{A,B\}_{q_0,t_0;q,t}$ by

$$\{A,B\}_{q_0,t_0;q,t}=\int_{t_0}^{t}dt'\int dq' A(q_0,t_0|q',t')B(q',t'|q,t), \quad (6)$$

and we shall omit the subscripts when there is no danger of confusion. The operation $\{A,B\}$ is associative, so that inner parentheses can be omitted:

$$\{\{A,B\},C\}=\{A,\{B,C\}\}\equiv\{A,B,C\}. \quad (7)$$

[7] If Eq. (5a) had also a solution G', we would have [in the notation explained in Eqs. (6) and (7)]

$$G'=G_\alpha-\{G'(V-V_\alpha),G_\alpha\},$$

and

$$\{G'(V-V_\alpha),G\}=\{G_\alpha(V-V_\alpha),G\}-\{G'(V-V_\alpha),G_\alpha(V-V_\alpha),G\},$$

and from Eq. (5),

$$\{G'(V-V_\alpha),G\}=\{G'(V-V_\alpha),G_\alpha\}-\{G'(V-V_\alpha),G_\alpha(V-V_\alpha),G\},$$

or

$$\{G_\alpha(V-V_\alpha),G\}=\{G'(V-V_\alpha),G_\alpha\};$$

and, therefore,

$$G-G_\alpha=G'-G_\alpha.$$

Any solution of (5a) is thus equal to any solution of (5), so that either equation can have only one solution.

In this notation, Eqs. (5) and (5a) are written as

$$G=G_\alpha-\{G_\alpha(V-V_\alpha),G\}, \quad (5')$$

$$G=G_\alpha-\{G(V-V_\alpha),G_\alpha\}. \quad (5a')$$

If, specially, V is the sum of pair potentials,

$$V=\sum_\beta V_\beta,$$

where the pairs are numbered by small Greek subscripts, and the sum extends over all pairs, Eq. (5) yields $N(N-1)/2$ integral equations for G:†

$$G=G_\alpha-\{G_\alpha\sum_{\beta,\beta\neq\alpha}V_\beta,G\}. \quad (8)$$

Another special case of Eq. (6) is the well-known equation

$$G=G_0-\{G_0V,G\}, \quad (9)$$

where G_0 is the principal solution of the Bloch equation for noninteracting particles; and of course one also has

$$G_\alpha=G_0-\{G_0V_\alpha,G_\alpha\}, \quad (10)$$

and the reverse equations corresponding to (5a).

From Eq. (8) it follows [with $V\equiv V(q_0)$] that†

$$VG=\sum_\alpha V_\alpha G=\sum_\alpha V_\alpha G_\alpha-\sum_{\alpha\neq\beta}\{V_\alpha G_\alpha V_\beta,G\}, \quad (11)$$

and

$$-\{G_0V,G\}=-\sum_\alpha\{G_0V_\alpha,G_\alpha\}+\sum_{\alpha\neq\beta}\{G_0,\{V_\alpha G_\alpha V_\beta,G\}\}. \quad (12)$$

With the notation

$$u_\alpha=G_\alpha-G_0=-\{G_0V_\alpha,G_\alpha\}=-\{G_\alpha V_\alpha,G_0\}, \quad (13)$$

one obtains, using Eqs. (9) and (10),

$$G-G_0=\sum_\alpha u_\alpha-\sum_{\alpha\neq\beta}\{u_\alpha V_\beta,G\}. \quad (14)$$

Successive substitution of Eq. (8) into this equation results in the binary collision expansion

$$G=G_0+\sum_\alpha u_\alpha-\sum_{\beta\neq\alpha}\{u_\alpha V_\beta,G_\beta\}+\sum_{\beta\neq\alpha,\gamma\neq\beta}\{u_\alpha V_\beta\{G_\beta V_\gamma,G_\gamma\}\}-\cdots. \quad (15)$$

In the notation of Huang, Lee, and Yang, our functions are given by

$$u_\alpha(q',t'|q,t)=U_2(\alpha_1',\alpha_2';\alpha_1,\alpha_2)\prod_{j\neq\alpha_1,\alpha_2}\prod_{j'\neq\alpha_1',\alpha_2'}U_1(j',j), \quad (16)$$

† The symbols $\sum_{\alpha\neq\beta}$, $\sum_{\alpha\neq\beta,\gamma\neq\beta}$, etc., are used for the sum over *all* indices, excluding the values $\alpha=\beta$, $\gamma=\delta$. Summation over β only, with $\beta\neq\alpha$, is indicated by $\sum_{\beta,\beta\neq\alpha}$.

where α_1, α_2 and α_1', α_2' stand for the coordinates of the two members of the pair α. We have (with $\hbar^2/2m=1$)

$$\left(\frac{\partial}{\partial t_0}+\sum_j \nabla_{0j}^2 - V_\alpha\right)G_\alpha=0, \quad (17)$$

or

$$\left(\frac{\partial}{\partial t_0}+\sum_j \nabla_{0j}^2\right)u_\alpha=V_\alpha G_\alpha, \quad (17')$$

where ∇_{0j}^2 acts on the components of q_0, so that

$$V_\alpha(q')G_\alpha(q',t'|q,t) = X(\alpha_1',\alpha_2';\alpha_1,\alpha_2) \prod_{j\neq\alpha_1,\alpha_2} \prod_{j'\neq\alpha_1',\alpha_2'} U_1(j',j), \quad (18)$$

in the notation of Huang, Lee, and Yang. This shows that the series (14) is identical with the binary collision expansion developed by these authors.

To show the equivalence of Eqs. (8) and (9) with the basic equations of Watson's formalism [Eqs. (26) of reference 4], we define the Laplace transform of our functions by

$$\int_{t_0}^{\infty} e^{-st}A(q_0, t_0|q, t_0+t)dt \equiv \langle q_0|A_L(s)|q\rangle. \quad (19)$$

Since all our functions depend only on $t-t_0$, the Laplace transform thus defined does not depend on t_0. The Laplace transform of $\{A,B\}$ is then the coordinate representation of the operator product A_LB_L. Equation (9) becomes

$$G_L=G_{0L}-G_{0L}\sum_\alpha V_\alpha G_L, \quad (20)$$

and Eqs. (8) and (10) after multiplication by $V_\alpha(q_0)$ become

$$V_\alpha G_L=V_\alpha G_{\alpha L}(1-\sum_{\beta,\beta\neq\alpha} V_\beta G_L), \quad (21)$$

$$V_\alpha G_{\alpha L}=V_\alpha G_{0L}(1-V_\alpha G_{\alpha L}), \quad (22)$$

where V_α is the operator whose coordinate representation is $V_\alpha(q_0)\delta(q-q_0)$. In Watson's notation we have, taking $s=-E$

$$G_{0L}(-E)=-(E-K)^{-1}, \quad (23)$$

where K is the operator of kinetic energy,

$$G_L(-E)=-\Omega(E-K)^{-1}, \quad (24)$$

$$V_\alpha G_{\alpha L}(-E)=-t_\alpha(E-K)^{-1}, \quad (25)$$

$$V_\alpha G_L(-E)=-t_\alpha\Omega_\alpha(E-K)^{-1}, \quad (26)$$

and our Eqs. (20), (21), and (22) become, after multiplication by $(E-K)$ from the right,

$$\Omega=1+(E-K)^{-1}\sum_\alpha t_\alpha\Omega_\alpha, \quad (27)$$

$$t_\alpha\Omega_\alpha=t_\alpha+t_\alpha(E-K)^{-1}\sum_{\beta,\beta\neq\alpha} t_\beta\Omega_\beta, \quad (28)$$

$$t_\alpha=V_\alpha+V_\alpha(E-K)^{-1}t_\alpha. \quad (29)$$

Taking the Laplace transform of Eq. (15) [with u_α substituted from Eq. (13)] yields

$$G_L=G_{0L}-\sum_\alpha G_{0L}V_\alpha G_{\alpha L}+\sum_{\beta\neq\alpha} G_{0L}V_\alpha G_{\alpha L}V_\beta G_{\beta L} - \sum_{\beta\neq\alpha,\gamma\neq\beta} G_{0L}V_\alpha G_{\alpha L}V_\beta G_{\beta L}V_\gamma G_{\gamma L}+\cdots, \quad (30)$$

or, with the notation introduced by Eqs. (23), (24), and (25),†

$$\begin{aligned}-G_L(-E)\equiv\Omega(E-K)^{-1}&=(E-K)^{-1} \\ &+\sum_\alpha(E-K)^{-1}t_\alpha(E-K)^{-1} \\ &+\sum_{\beta\neq\alpha}(E-K)^{-1}t_\alpha(E-K)^{-1}t_\beta(E-K)^{-1} \\ &+\sum_{\beta\neq\alpha,\gamma\neq\beta}(E-K)^{-1}t_\alpha(E-K)^{-1}t_\beta(E-K)^{-1}t_\gamma(E-K)^{-1} \\ &+\cdots. \end{aligned} \quad (31)$$

Comparison with Eq. (27) of reference 4 shows that the binary collision expansion is the Laplace inverse of the coordinate representation of the scattering operator expansion multiplied from the right by $-(E-K)^{-1}$.