Direct Calculation of Second-Order Density Matrix

I. Theory of the Green's Function Technique[*]

by

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ABSTRACT

We present a method for directly determining the second-order density matrix of a system of particles with pairwise additive interactions. The result is obtained as a contour integral involving the two-particle Green's function. The random phase approximation is made and the evaluation of the Green's function is reduced to a simple matrix problem. An outline of the computational method is presented, and possible applications are discussed.

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I. Introduction

In this paper we show how to obtain directly the second-order density matrix of a system of pairwise interacting Fermi particles. We employ the Green's function method, which has recently[1] been used to calculate the first-order density matrix of the helium atom. The important advantage of this technique is that it permits the direct calculation of reduced quantities; it does not require the calculation of the N-particle wave function.

In Sec. II we demonstrate the connection between the two-particle Green's function $\mathscr{G}$ and the second-order density matrix Γ. The usual time-dependent perturbation treatment of the wave function and an introduction to the use of diagrams is presented in Sec. III. In Sec. IV we use Green's function diagrams to derive an exact integral equation for $\mathscr{G}$. Approximations to the so-called irreducible vertex potential are also introduced. We obtain a matrix equation for the Green's function in Sec. V using the random phase approximation to the irreducible vertex potential. The second-order density matrix is then obtained from $\mathscr{G}$ by performing a contour integral. One contribution to this integral is evaluated analytically, but there remains a contribution which must be done numerically. Finally we discuss the application of these methods to problems of interest.

II. Second-Order Density Matrix and Two-Particle Green's Function

The two-particle propogator (Green's function) $\mathscr{G}$ corresponding to the state vector $|\Psi\rangle$ is written in the Heisenberg representation as follows:

$$\mathcal{G}(1,2,3,4|t-t') = \frac{1}{i^2}\,\frac{{}_H\langle\Psi|T\,\psi_H(1t)\,\psi_H(2t)\,\psi_H^\dagger(3t')\,\psi_H^\dagger(4t')|\Psi\rangle_H}{{}_H\langle\Psi|\Psi\rangle_H}, \tag{II.1}$$

where ψ_H^+ and ψ_H are Fermion[2] field creation and annihilation operators respectively, T is the time ordering operator, and the integers 1, 2, 3, 4, refer to space-spin coordinates. The fact that $\mathcal{G}$ depends only on the difference t-t' can be seen easily, by recalling that we are in the Heisenberg picture (thus the subscript H). The denominator of Eq. (II.1) is included so that we can obtain a linked diagram expansion for $\mathcal{G}$. This will become clear in Sec. IV.

The second-order density matrix Γ belonging to the state vector $|\Psi>$ is given in second-quantization notation by

$$\Gamma(1,2,1',2') = \frac{{}_H\langle\Psi|\,\psi_H^\dagger(1't)\,\psi_H^\dagger(2't)\,\psi_H(2t)\,\psi_H(1t)|\Psi\rangle_H}{{}_H\langle\Psi|\Psi\rangle_H}. \tag{II.2}$$

Thus we find that we can express Γ in terms of $\mathcal{G}$:

$$\Gamma(1,2,1',2') = -\lim_{t'\to t_+} \mathcal{G}(1,2,1',2'|t-t'), \tag{II.3}$$

where the antisymmetry of Γ and $\mathcal{G}$[3] has been used, and the limit is taken as t' approaches t from above (t' > t). The minus sign is due to the presence of the time ordering operator T .

In the following sections, we will obtain an expression not for $\mathcal{G}$(t-t') but rather for its fourier transform $\mathcal{G}$(E) defined in the following equation:

$$\mathcal{G}(1,2,3,4|t-t') = \frac{1}{2\pi}\int_{-\infty}^{\infty} e^{-iE(t-t')}\,\mathcal{G}(1,2,3,4|E)\,dE . \qquad \text{(II.4)}$$

With this, Eq. (II.3) becomes

$$\Gamma(1,2,1',2') = -\frac{1}{2\pi}\lim_{\tau\to 0+}\int_{-\infty}^{\infty} e^{iE\tau}\,\mathcal{G}(1,2,3,4|E)\,dE . \qquad \text{(II.5)}$$

This integral can be evaluated as a contour integral in the upper half complex E plane (Fig. I). The upper half plane is chosen so that the integral over the arc vanishes due to the factor $e^{-\tau(\mathrm{Im}E)}$. We will see later that $\mathcal{G}$ (E) has poles both above the real axis to the left of the imaginary axis, and below the real axis to the right of the imaginary axis, as is shown in Fig. (I). Because the integral about contour 1 is difficult to do, we choose instead the contour shown in Fig. (II). Both contour 1 and contour 2 enclose the same poles of $\mathcal{G}$ (E) and so they lead to the same result when substituted into Eq. (II.5). We choose the Coulson contour because the integral over the arc ($E = Re^{i\theta}$, $\frac{\pi}{2} \leq \theta \leq \frac{3\pi}{2}$) can be done analytically and the integral

<u>Figure I.</u> Contour 1

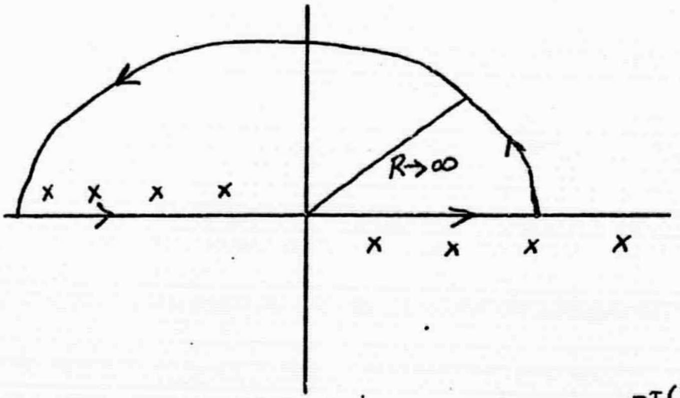
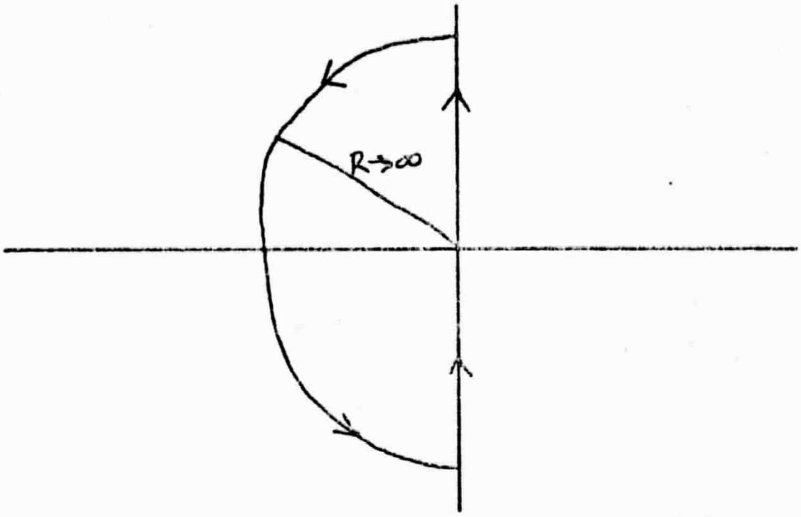


Figure II. Coulson Contour[7]



along the imaginary axis can be handled conveniently by standard numerical techniques.

Therefore we reduce the problem of calculating the second-order density matrix Γ to that of finding an expression for $\mathcal{G}(E)$ and then evaluating the contour integral:

$$\Gamma(1,2,1',2') = -\frac{i}{2\pi} \lim_{R\to\infty} \left\{ \int_{\frac{\pi}{2}}^{\frac{3\pi}{2}} \mathcal{G}(1,2,1',2'|Re^{i\theta})\, Re^{i\theta}\, i\, d\theta \right.$$

$$\left. + \int_{-R}^{R} \mathcal{G}(1,2,1',2'|iy)\, i\, dy \right\}. \tag{II.6}$$

The evaluation of these two integrals will be treated in Sec. IV.

III. Time-dependent Perturbation Expansion of $|\Psi>$ and Diagrams

We assume that the hamiltonian of our system is written as

$$H(t) = H^\circ + e^{-\alpha|t|} V \tag{III.1a}$$

where H^O is a sum of one-particle hamiltonians (perhaps Hartree-Fock or hydrogenic), and V is a two-particle time-independent perturbation:

$$H^\circ = \sum_{i=1}^{N} h(i) ,$$

$$V = \sum_{i<j=1}^{N} V(i,j) . \tag{III.1b}$$

We also assume that we know the eigenfunctions of h, and thus of H^C.

The time-dependent Schrödinger equation is written as follows:

$$i\hbar \frac{\partial|\Psi(t)\rangle}{\partial t} = H(t)\,|\Psi(t)\rangle . \tag{III.2}$$

However, the problem is not yet completely specified. We must also stipulate the state vector $|\Psi>$ at some time. Therefore we decide that at $t = -\infty$, $|\Psi>$ is given by some eigenfunction of H^O,

$$|\Psi(t=-\infty)\rangle = |\Phi\rangle \tag{III.3}$$

where

$$H^\circ|\Phi\rangle = E^\circ|\Phi\rangle . \tag{III.4}$$

The vector $|\Phi>$ will usually be some Slater determinant of spin-orbitals which are eigenfunctions of h .

To write the Schrödinger equation in a more useful form, we transform to the interaction representation. This is done by defining new state vectors and operators as follows:

$$|\Psi(t)\rangle_I = e^{\frac{i}{\hbar}H^0 t}|\Psi(t)\rangle \tag{III.5a}$$

$$V_I(t) = e^{-\alpha|t|}\, e^{\frac{i}{\hbar}H^0 t}\, V\, e^{-\frac{i}{\hbar}H^0 t} \tag{III.5b}$$

$$H^0_I(t) = e^{\frac{i}{\hbar}H^0 t}\, H^0\, e^{-\frac{i}{\hbar}H^0 t} = H^0 . \tag{III.5c}$$

The Schrödinger equation and its boundary condition in this representation now become

$$\begin{gathered} i\hbar \frac{\partial}{\partial t}|\Psi(t)\rangle_I = V_I(t)|\Psi(t)\rangle_I \\ |\Psi(t=-\infty)\rangle_I = |\Phi\rangle . \end{gathered} \tag{III.6}$$

This is equivalent to the following integral equation

$$|\Psi(t)\rangle_I = |\Phi\rangle - \frac{i}{\hbar}\int_{-\infty}^{t} dt_1\, V_I(t_1)|\Psi(t_1)\rangle_I , \tag{III.7}$$

which can be iterated to yield the usual perturbation expression for $|\Psi(t)>_I$

$$
\begin{aligned}
|\Psi(t)\rangle_I &= |\Phi\rangle + \frac{-i}{\hbar}\int_{-\infty}^{t} dt_1\, V_I(t_1)\,|\Phi\rangle \\
&+ \left(\frac{-i}{\hbar}\right)^2 \frac{1}{2!}\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2\, T\, V_I(t_1)\, V_I(t_2)\,|\Phi\rangle + \cdots \\
&+ \left(\frac{-i}{\hbar}\right)^n \frac{1}{n!}\int_{-\infty}^{t} dt_1 \cdots \int_{-\infty}^{t} dt_n\, T\, V_I(t_1)\, V_I(t_2) \cdots V_I(t_n)\,|\Phi\rangle + \cdots . \qquad \text{(III.8)}
\end{aligned}
$$

The time ordering operator T arises by recognizing the identity

$$
n!\int_{-\infty}^{t} dt_1 \int_{-\infty}^{t_1} dt_2 \cdots \int_{-\infty}^{t_{n-1}} dt_n\, V_I(t_1)\, V_I(t_2) \cdots V_I(t_n) = \int_{-\infty}^{t} dt_1 \int_{-\infty}^{t} dt_2 \cdots \int_{-\infty}^{t} dt_n\, T\, V_I(t_1) \cdots V_I(t_n) \qquad \text{(III.9)}
$$

For convenience we write Eq. (III.8) formally in the form

$$
\begin{aligned}
|\Psi(t)\rangle_I &= U_I(t,-\infty)\,|\Phi\rangle \\
&= \left(1 + U_I^{(1)} + U_I^{(2)} + \cdots U_I^{(n)} + \cdots\right)|\Phi\rangle, \qquad \text{(III.10)}
\end{aligned}
$$

where we have made the (obvious) identification of terms in Eq. (III.8) involving m-V_I's with $U_I^{(m)}$. Because we are interested in obtaining an eigenfunction of $H^0 + V$, we integrate from $-\infty$ to 0 and we take the adiabatic ($\alpha \to 0$) limit of the terms in Eq. (III.8).

It may seem that the introduction of the time ordering operator T accomplished nothing, but as can be seen by reading any book on many-body theory, its presence is essential to the use of Wick's theorem and the techniques of Feynman diagrams.[4]

To illustrate the use of diagrams in expressing the terms given in Eq. (III.8) we consider the first order contribution $U_I^{(1)}(0,-\infty)|\Phi\rangle$.

This can be written in second quantization notation as

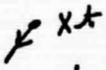
$$-\frac{i}{\hbar}\,\frac{1}{2}\int_{-\infty}^{0} dt_1 \iint d1\,d2\, T e^{-\alpha|t_1|}\, v\, \psi_I^+(1t_1)\,\psi_I^+(2t_1)\,\psi_I(2t_1)\,\psi_I(1t_1)|\Phi\rangle. \qquad \text{(III.11)}$$

Each field operator is written in the particle-hole picture as

$$\psi^+ = \psi_+^+ + \psi_-^+$$
$$\psi = \psi_+ + \psi_-$$

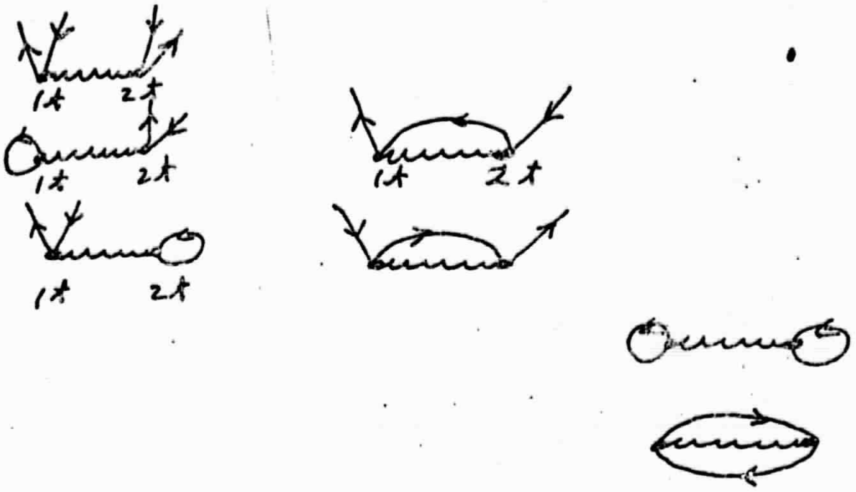
and each of the particle-hole operators is represented by a directed line segment as in Fig. (III).

Figure III

$\psi_+^+(xt)$		particle creation
$\psi^+(xt)$		hole annihilation
$\psi_+(xt)$		hole creation
$\psi_-(xt)$		particle annihilation

In these diagrams, time increases in the positive vertical direction. Recalling that in the particle-hole picture the unperturbed vector $|\Phi\rangle$ becomes the vacuum state represented by $|0\rangle$, we find by using Wick's theorem that the contributions to (III.11) can be written diagramatically as in Fig. (IV).

Figure IV



The wavy line represents V(1,2). The construction and use of such diagrams is discussed in a number of texts,[2] and so we will pursue it no more here. In the next section we will use somewhat different diagrams (Green's function diagrams) to derive an integral equation for the exact two-particle Green's function.

IV. Evaluation of Two-Particle Green's Function

The expression given in Eq. (II.1) for the exact two-particle Green's function $\mathcal{G}$ can be rewritten in a form more amenable to calculation by using the following relations between the Heisenberg and interaction pictures:

$$|\Psi\rangle_H = |\Psi(t=0)\rangle_I = U_I(0,-\infty)\,|\Phi\rangle \qquad \text{(IV.1a)}$$

and

$$\psi_H(1t) = U_I(0,t)\,\psi_I(1t)\,U_I(t0) \qquad \text{(IV.1b)}$$

$$\psi_H^+(1t) = U_I(0,t)\,\psi_I^+(1t)\,U_I(t0)\ . \qquad \text{(IV.1c)}$$

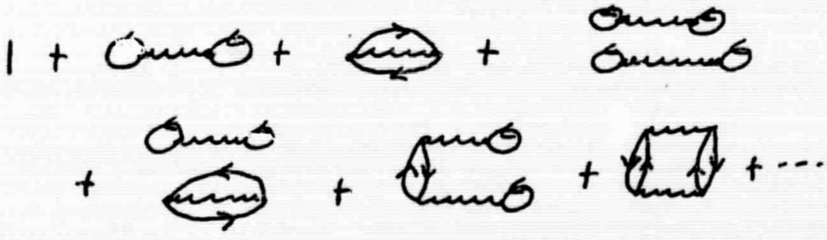
These relations lead to the following expression for $\mathcal{G}$:

$$\mathcal{G}(1,2,3,4|t-t') = \frac{1}{i^2}\,\frac{\langle\Phi|T\,U(\infty,t)\,\psi(1t)\,\psi(2t)\,U(t,t')\,\psi^+(3t')\,\psi^+(4t')\,U(t',-\infty)|\Phi\rangle}{\langle\Phi|U(\infty,-\infty)|\Phi\rangle} \qquad \text{(IV.2)}$$

where the subscript (I) has been dropped for convenience.

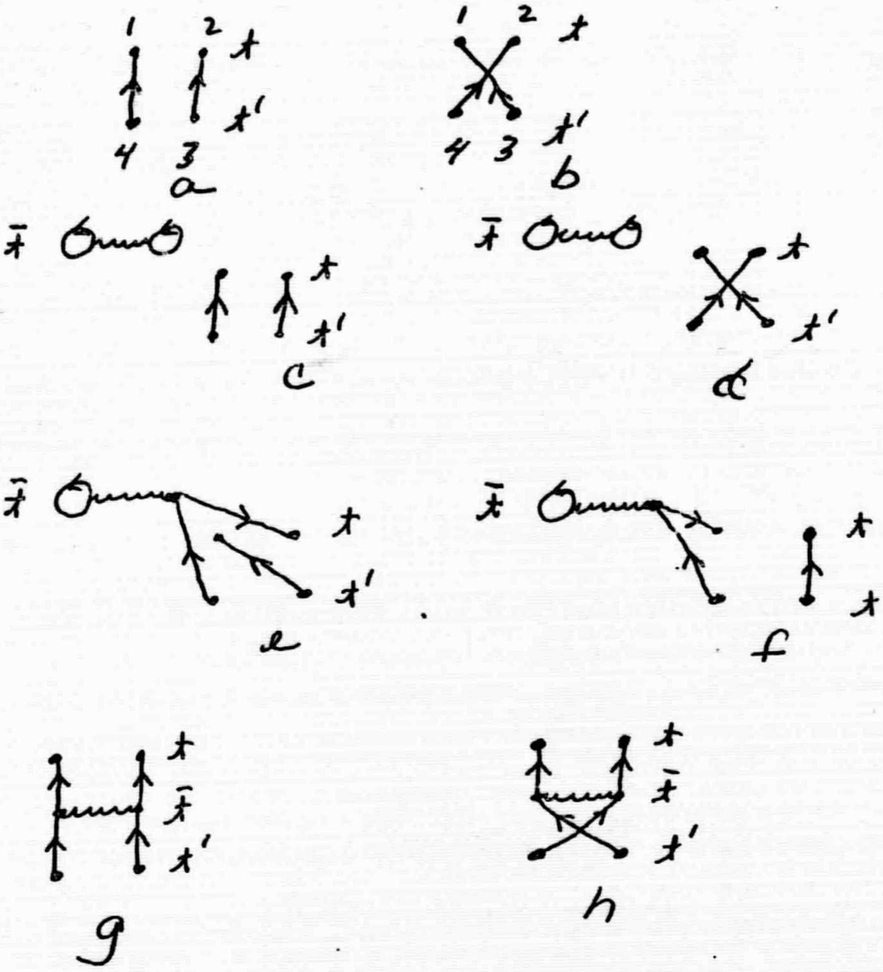
The denominator in Eq. (IV.2) can be expressed as the sum of all time integrated vacuum diagrams, some of which are shown in Fig. (V).

Figure V

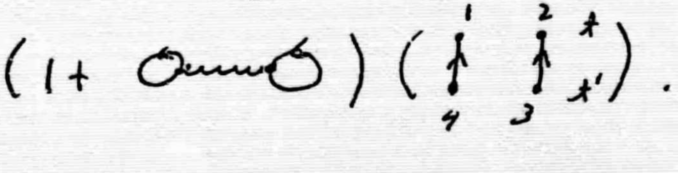


The numerator must be expressed in terms of the so called Green's function diagrams. These diagrams are obtained by expanding as in Eq. (III.10) each of the three U's appearing in the numerator and then using techniques similar to those used in writing the diagrams in Fig. (IV). Some of the Green's function diagrams are shown in Fig. (VI).

Figure VI



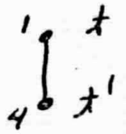
In these diagrams all time orderings of $\bar{t}$ with respect to t and t' are implied. Thus disconnected diagrams such as in c) and d) will factor into their constituent parts. Then, for example, diagrams a) and c) can be combined to give



If higher order diagrams were included in Fig. (VI), we would find that much factorization of diagrams would occur and that the above result would generalize to

But this first factor is exactly what we wrote in Fig. (V) for the denominator. This type of factorization occurs for all disconnected diagrams, and thus we can omit such diagrams from the list of Green's function diagrams since they only serve to cancel the denominator.

Diagrams a) and b) represent the unperturbed two-particle Green's function $\mathcal{G}^{0}$. Each directed line segment represents and unperturbed one-particle Green's function G^{0}



$$= G^{0}(1,4,t-t'),$$

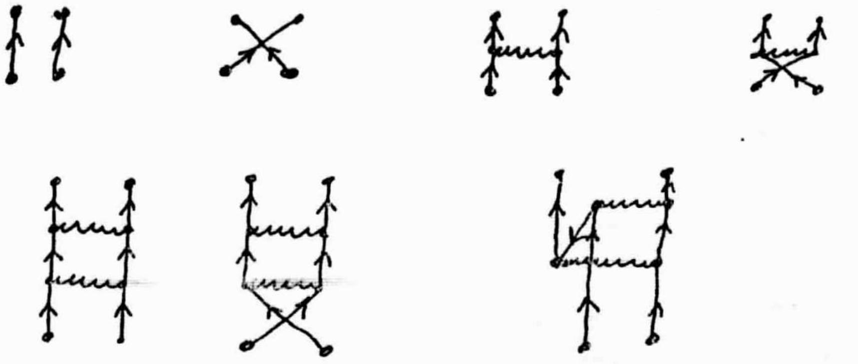
and so diagrams a) and b) yield

$$\mathcal{G}^{0}(1,2,3,4|t-t') = G^{0}(1,4,t-t')G^{0}(2,3,t-t') - G^{0}(1,3,t-t')G^{0}(2,4,t-t'). \tag{IV.3}$$

Diagrams such as e) and f) convert the unperturbed G^{0} into the exact one-particle Green's function G. Therefore we can omit diagrams in which the section containing the wavy line(s) is connected to only one of the directed line segments if we now interpret directed line segments to represent not G^{0} but the exact G.

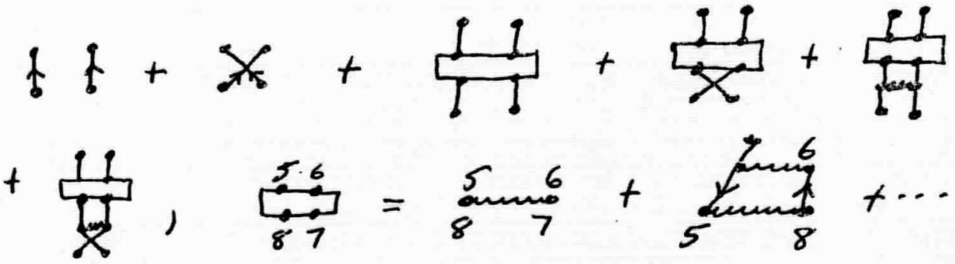
With these considerations we can write the essential diagrams which contribute to $\mathcal{G}$. Some of these are given in Fig. (VII).

Figure VII



To understand how these diagrams lead to an integral equation for $\mathcal{G}$ we have written them in slightly different form in Fig. (VIII).

Figure VIII



The box represents a generalized potential which is non-local in space and time. We recognize that the sum of the diagrams which are attached to the bottom of the box is identical to the sum of the Green's function diagrams given in Fig. (VII). From this rather sketchy development we now write the following integral equation for $\mathcal{G}$:

$$\mathcal{G}(1,2,3,4|t-t') = G(1,4,t-t')G(2,3,t-t')$$
$$- G(1,3,t-t')G(2,4,t-t') + \int G(1,6,t-\bar{t})G(2,5,t-\bar{t})$$
$$\bar{V}(5,6,7,8,\bar{t}-\bar{t}')\mathcal{G}(7,8,3,4|\bar{t}'-t')\, d5\, d6\, d7\, d8\, d\bar{t}\, d\bar{t}', \tag{IV.4}$$

where $\bar{V}$, which is represented by the box in Fig. (VIII), is commonly referred to as the irreducible vertex potential. We can think of $\bar{V}$ as the potential describing the interaction between two particles moving in the "sea" of the remaining particles.

The irreducible vertex potential can be evaluated to any desired order by simply writing all Green's function diagrams of that order and then identifying the contributions to $\bar{V}$ as that which multiplies the factor

$$G(1,6,t-\bar{t})G(2,5,t-\bar{t})\Big[G(7,4,\bar{t}'-t')G(8,3,\bar{t}'-t')$$
$$- G(7,3,\bar{t}'-t')G(8,4,\bar{t}'-t')\Big].$$

To see this we expand $\mathcal{G}$ and $\bar{V}$ in a perturbation series and then write Eq. (IV.4) in symbolic notation

$$\mathcal{G} = \mathcal{G}^{(0)} + \mathcal{G}^{(1)} + \mathcal{G}^{(2)} + \cdots \tag{IV.5a}$$

$$\bar{V} = \bar{V}^{(0)} + \bar{V}^{(2)} + \cdots \tag{IV.5b}$$

$$\mathcal{G}^{(0)} = [GG - GG] \qquad \text{(IV.5c)}$$

$$\mathcal{G}^{(1)} = \int GG\,\bar{V}^{(1)}[GG-GG] \qquad \text{(IV.5d)}$$

$$\mathcal{G}^{(2)} = \int GG\,\bar{V}^{(1)}\mathcal{G}^{(1)} + \int GG\,\bar{V}^{(2)}[GG-GG] \qquad \text{(IV.5e)}$$

$$\int GG\,\bar{V}^{(1)}\mathcal{G}^{(1)} = \int GG\,\bar{V}^{(1)}\int GG\,\bar{V}^{(1)}[GG-GG] \qquad \text{(IV.5f)}$$

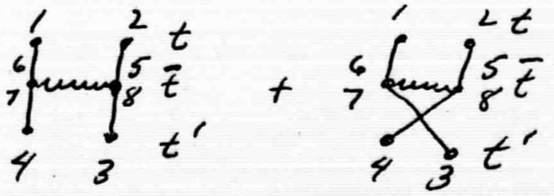
etc.

Thus we see that we can identify $\bar{V}^{(1)}$ as that factor which multiplies GG[GG−GG] in the first order diagrams; likewise $\bar{V}^{(2)}$ is the factor multiplying GG[GG−GG] in the second order diagrams. This result can obviously be generalized to higher orders. As an example, let us consider the first order contribution to $\bar{V}$:

$$\mathcal{G}^{(1)} = \int G(1,6,t-\bar{t})\,G(2,5,t-\bar{t})\,\bar{V}^{(1)}(5,6,7,8,\bar{t}-\bar{t}')$$

$$[G(7,4,\bar{t}'-t')\,G(8,3,\bar{t}'-t') - G(7,3,\bar{t}'-t')\,G(8,4,\bar{t}'-t')]. \qquad \text{(IV.6)}$$

From the first order diagrams we obtain



which equals

$$i \int G(1,6,t-\bar{t})\, G(2,5,t-\bar{t})\, V(5-6) \left[G(6,4,\bar{t}-t')\, G(5,3,\bar{t}-t') - G(6,3,\bar{t}-t')\, G(5,4,\bar{t}-t') \right].$$

Therefore, we identify $\bar{V}^{(1)}$ as

$$\bar{V}^{(1)}(5,6,7,8,\bar{t}-\bar{t}') = i\,\delta(\bar{t}-\bar{t}')\,\delta(5-8)\,\delta(6-7)\,V(5-6). \qquad \text{(IV.7)}$$

Higher order terms are calculated in a similar fashion.

In the next section we will develop Eq. (IV.4) in more detail by using only the first order irreducible vertex potential given by Eq. (IV.7). This approximation will be referred to as the random phase approximation (RPA).[5]

V. RPA in a Basis

Substituting the random phase approximation for the irreducible vertex potential into the exact Eq. (IV.5), we arrive at the following approximate equation

$$\mathcal{G}(1,2,3,4/t-t') = G(1,4,t-t')\, G(2,3,t-t') - G(1,3,t-t')\, G(2,4,t-t') + i \int G(1,6,t-\bar{t})\, G(2,5,t-\bar{t})\, V(5-6)\, \mathcal{G}(6,5,3,4/\bar{t}-t')\, d5\, d6\, d\bar{t}. \qquad \text{(V.1)}$$

We now assume that the fourier transform of the exact one-particle Green's function is known and is given in the form:[6]

$$G(1,4,E) = \sum_{\alpha=1}^{P_1} g_\alpha (E - E_\alpha^+)^{-1} \phi_\alpha(1) \phi_\alpha^*(4)$$

$$+ \sum_{S=P_1+1}^{P} g_s (E - E_s^-)^{-1} \phi_s(1) \phi_s^*(4) , \tag{V.2}$$

where the g_i, E_α^+, and E_s^- are c-numbers with

$$E_\alpha^+ = E_\alpha + i\epsilon \tag{V.3a}$$

$$E_s^- = E_s - i\epsilon \tag{V.3b}$$

The number P_1 and the Greek and Roman subscripts are used in the summations to distinguish between those poles which lie above the real axis (E_α^+) and those which lie below (E_s^-). The (not necessarily linearly independent) functions ϕ_i are assumed to be expanded in some chosen basis set of spin-orbitals $\{\chi_a\}$ as

$$\phi_i(1) = \sum_{a=1}^{M} C_{ia} \chi_a(1) , \tag{V.4}$$

and C_{ia} are assumed known.

The time-dependent one-particle Green's function can be obtained by fourier transform from Eq. (V.2). This gives the following result:

$$G(1,4,t-t') = \Theta(t-t') G_+(1,4,t-t') + \Theta(t'-t) G_-(1,4,t-t') , \tag{V.5}$$

where we have defined

$$G_-(1,4,t-t') = \frac{-1}{i}\sum_{\alpha=1}^{P_1} g_\alpha \phi_\alpha(1)\phi_\alpha^*(4)\, e^{-iE_\alpha^+(t-t')} \tag{V.6a}$$

$$G_+(1,4,t-t') = \frac{1}{i}\sum_{s=P_1+1}^{P} g_s \phi_s(1)\phi_s^*(4)\, e^{-iE_s^-(t-t')}, \tag{V.6b}$$

and $\Theta(t)$ is the unit step function.

With this, we can rewrite Eq. (V.1) as

$$\begin{aligned}\mathcal{G}(1,2,3,4|t-t') &= \Theta(t-t')\,[G_+(1,4,t-t')\,G_+(2,3,t-t') - \\ &G_+(1,3,t-t')\,G_+(2,4,t-t')] + \Theta(t'-t)\,[G_-(1,4,t-t')\,G_-(2,3,t-t') \\ &- G_-(1,3,t-t')\,G_-(2,4,t-t')] \quad + i\int\{\Theta(t-\bar{t}) \\ &G_+(1,6,t-\bar{t})\,G_+(2,5,t-\bar{t}) + \Theta(t'-t)\,G_-(1,6,t-\bar{t})\,G_-(2,5,t-\bar{t})\} \\ &V(5-6)\,\mathcal{G}(6,5,3,4|\bar{t}-t')\,d\bar{t}\,d5\,d6\end{aligned} \tag{V.7}$$

We fourier transform this equation to yield a more useful result:

$$\begin{aligned}\mathcal{G}(1,2,3,4|E) &= (1-P_{34})\,G(1,2,3,4|E) + \\ &i\int G(1,2,5,6|E)\,V(5-6)\,\mathcal{G}(6,5,3,4|E)\,d5\,d6,\end{aligned} \tag{V.8}$$

where we have defined G(1,2,3,4|E) as the fourier transform of G(1,4,t-t') G(2,3,t-t'). Let us now examine the permutation symmetry of factors in Eq. (V.8), remembering that $\mathcal{G}(1,2,3,4|E)$ is antisymmetric in variables (1,2) and (3,4).

First consider the integral term:

$$
\begin{aligned}
&P_{12}\int G(1,2,5,6|E)\, i\, V(5-6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 \\
&= \int G(2,1,5,6|E)\, i\, V(5-6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 \\
&= \int G(1,2,6,5|E)\, i\, V(5-6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 \\
&= \int G(1,2,5,6|E)\, i\, V(5-6)\, \mathcal{G}(5,6,3,4|E)\, d5\, d6 \\
&= -\int G(1,2,5,6|E)\, i\, V(5-6)\, \mathcal{G}(6,5,3,4|E)\, d5\, d6 .
\end{aligned}
\qquad (V.9)
$$

We have used the fact that G(1,2,3,4|E) is the fourier transform of the product G(1,4,t) G(2,3,t), and we recognized that the variables (5,6) are dummy. Thus the integral term is antisymmetric in variables (1,2) and (3,4). Therefore the first term in Eq. (V.8) must also be antisymmetric in (1,2) and (3,4).

Hence we can expand Eq. (V.8) in the following basis of antisymmetric functions:

$$[ab](1,2) = \frac{1}{\sqrt{2}}\left(\chi_a(1)\chi_b(2) - \chi_a(2)\chi_b(1)\right) . \qquad (V.10)$$

This results in the matrix equation given below:

$$\mathcal{G}_{ab,cd}(E) = G_{ab,cd}(E) - \sum_{\substack{e<f \\ g<h \\ =1}}^{M} G_{ab,ef}(E)\,(ef|V|\widetilde{gh})\,\mathcal{G}_{gh,cd}(E). \qquad (V.11)$$

We have made the following identifications:

$$\mathcal{G}(1,2,3,4|E) = \sum_{\substack{a<b \\ c<d \\ =1}}^{M} \frac{1}{2}\,\mathcal{G}_{ab,cd}(E)\,[ab](1,2)\,[cd]^{*}(3,4) \qquad (V.12a)$$

$$G_{ab,cd}(E) = \sum_{s,t=P_1+1}^{P} g_s g_t (E-E_s-E_t)^{-1} C_{sa} C_{tb} C^{*}_{tc} C^{*}_{sd}$$

$$-\sum_{\alpha,\beta=1}^{P_1} g_\alpha g_\beta (E-E_\alpha-E_\beta)^{-1} C_{\alpha a} C_{\beta b} C^{*}_{\beta c} C^{*}_{\alpha d} \qquad (V.12b)$$

and

$$(ef|v|\widetilde{gh}) = \int \chi_e(1)\chi_f(2)\,V(1-2)\,[\chi_g(1)\chi_h(2) - \chi_g(2)\chi_h(1)]^{*}\,d1\,d2. \qquad (V.12c)$$

Thus given any basis $\{\chi_a,\ a = 1\cdots M\}$ and the exact one-particle Green's function as in Eq. (V.2), we can calculate the matrix elements $G_{ab,cd}(E)$ (for any E) and $(ef|v|\widetilde{gh})$. Eq. (V.11) is then a simple matrix equation which determines $\mathcal{G}_{ab,cd}(E)$. We write this equation in matrix form as

$$\underset{\sim}{\mathcal{G}}(E) = \underset{\sim}{G}(E) - \underset{\sim}{G}(E)\,\underset{\sim}{V}\,\underset{\sim}{\mathcal{G}}(E), \qquad (V.13)$$

from which it follows that

$$\underset{\sim}{\mathcal{G}}(E) = [\underset{\sim}{G}^{-1}(E) + \underset{\sim}{V}]^{-1}. \qquad (V.14)$$

This is the final expression for $\mathcal{G}(E)$.

Let us now return to the problem of evaluating the second-order density matrix as discussed in section II. Being careful to notice the 1/i in Eq. (V.12a), we write the previous expression for Γ in matrix notation as follows:

$$\underset{\sim}{\Gamma} = -\frac{1}{2\pi i} \lim_{R\to\infty} \left\{ \int_{\frac{\pi}{2}}^{\frac{3\pi}{2}} \underset{\sim}{G}(Re^{i\theta})\, Re^{i\theta}\, i\, d\theta + \int_{-R}^{R} \underset{\sim}{G}(iy)\, i\, dy \right\}, \tag{V.15}$$

with $\underset{\sim}{\Gamma}$ being defined by

$$\Gamma(1,2,1',2') = \sum_{\substack{a<b \\ c<d=1}}^{M} \Gamma_{ab,cd}\, [ab](1,2)\, [cd]^{*}(1',2') \tag{V.16}$$

The evaluation of the arc integral can be done analytically by noticing (see Eq. (V.12b)) that for large R we have

$$G_{ab,cd}(Re^{i\theta}) = (Re^{i\theta})^{-1} \left\{ \sum_{s,t=p_1+1}^{p} g_s g_t C_{sa} C_{tb} C^{*}_{tc} C^{*}_{sd} - \sum_{\alpha,\beta=1}^{p_1} g_\alpha g_\beta C_{\alpha a} C_{\beta b} C^{*}_{\beta c} C^{*}_{\alpha d} \right\},$$

$$\equiv (Re^{i\theta})^{-1} B_{ab,cd}. \tag{V.17}$$

This defines the matrix $\underset{\sim}{B}$. Therefore the arc integral reduces to

$$\underset{\sim}{\Gamma}_{arc.} = -\frac{1}{2\pi i} \lim_{R\to\infty} \int_{\frac{\pi}{2}}^{3\pi/2} \left[Re^{i\theta} \underset{\sim}{B}^{-1} + \underset{\sim}{V}\right]^{-1} Re^{i\theta} i \, d\theta$$

$$= -\frac{1}{2\pi} \int_{\frac{\pi}{2}}^{\frac{3\pi}{2}} \underset{\sim}{B} \, d\theta$$

$$= -\frac{1}{2} \underset{\sim}{B} . \qquad (V.18)$$

This result is exact.

To evaluate the integral along the imaginary axis we must resort to the use of numerical integration techniques. However we should at least write the integral in a form which is most amenable to computer treatment. First we note that each term in $\mathcal{G}_{ab,cd}(iy)$ contains factors of the form

$$(iy - E_s - E_t)^{-1} = -\left(y^2 + (E_s + E_t)^2\right)^{-1} (E_s + E_t + iy) . \qquad (V.19)$$

Therefore we can write $\underset{\sim}{G}(iy)$ as

$$\underset{\sim}{G}(iy) = \underset{\sim}{G}^{(1)}(y) + i \underset{\sim}{G}^{(2)}(y)$$

where

$$G^{(1)}_{ab,cd}(y) = -\sum_{s,t=P_1+1}^{P} g_s g_t (E_s + E_t)\left(y^2 + (E_s + E_t)^2\right)^{-1}$$
$$C_{sa} C_{tb} C^{\dagger}_{tc} C^{\dagger}_{sc} + \sum_{\alpha,\beta=1}^{P_1} g_\alpha g_\beta (E_\alpha + E_\beta)\left(y^2 + (E_\alpha + E_\beta)^2\right)^{-1} \qquad (V.20a)$$
$$C_{\alpha a} C_{\beta b} C^{\dagger}_{\beta c} C^{\dagger}_{\alpha d} ,$$

and

$$G^{(2)}_{ab,cd}(y) = -\sum_{s,t=p_1+1}^{p} g_s g_t \, y \, (y^2+(E_s+E_t)^2)^{-1} C_{sa} C_{tb} C^*_{tc} C^*_{sd}$$

$$+\sum_{\alpha,\beta=1}^{p_1} g_\alpha g_\beta \, y \, (y^2+(E_\alpha+E_\beta)^2)^{-1} C_{\alpha a} C_{\beta b} C^*_{\beta c} C^*_{\alpha d} . \qquad \text{(V.20b)}$$

We also decompose $\underset{\sim}{G}^{-1}(iy)$ and $\underset{\sim}{\mathcal{G}}(iy)$ into real and imaginary components as

$$\underset{\sim}{G}^{-1}(iy) = \underset{\sim}{T}(y) + i \, \underset{\sim}{U}(y) \qquad \text{(V.21a)}$$

and

$$\underset{\sim}{\mathcal{G}}(iy) = \underset{\sim}{\mathcal{G}}^{(1)}(y) + i \, \underset{\sim}{\mathcal{G}}^{(2)}(y) . \qquad \text{(V.21b)}$$

To determine $\underset{\sim}{T}(y)$ and $\underset{\sim}{U}(y)$ we write

$$(\underset{\sim}{G}^{(1)}(y) + i \, \underset{\sim}{G}^{(2)}(y))(\underset{\sim}{T}(y) + i \, \underset{\sim}{U}(y)) = \underset{\sim}{1} \qquad \text{(V.22)}$$

in real and imaginary parts. This results in the following matrix equations:

$$\underset{\sim}{T}(y) = [\underset{\sim}{G}^{(1)}(y) + \underset{\sim}{G}^{(2)}(y) \, \underset{\sim}{G}^{(1)^{-1}}(y) \, \underset{\sim}{G}^{(2)}(y)]^{-1} \qquad \text{(V.23a)}$$

and

$$\underset{\sim}{U}(y) = - \underset{\sim}{G}^{(1)^{-1}}(y) \, \underset{\sim}{G}^{(2)}(y) \, \underset{\sim}{T}(y) . \qquad \text{(V.23b)}$$

Then knowing $\underset{\sim}{T}(y)$ and $\underset{\sim}{U}(y)$ we can write Eq. (V.14) as

$$\left[\underset{\sim}{T}(y) + i\,\underset{\sim}{U}(y) + \underset{\sim}{V}\right]\left[\underset{\sim}{\mathcal{G}}^{(1)}(y) + i\,\underset{\sim}{\mathcal{G}}^{(2)}(y)\right] = \underset{\sim}{1}$$

which yields equations for $\underset{\sim}{\mathcal{G}}^{(1)}(y)$ and $\underset{\sim}{\mathcal{G}}^{(2)}(y)$:

$$\underset{\sim}{\mathcal{G}}^{(1)}(y) = \left[(\underset{\sim}{T}(y) + V) + \underset{\sim}{U}(y)(\underset{\sim}{T}(y) + \underset{\sim}{V})^{-1} U(y)\right]^{-1} \tag{V.24a}$$

$$\underset{\sim}{\mathcal{G}}^{(2)}(y) = -\,(\underset{\sim}{T}(y) + \underset{\sim}{V})^{-1}\,\underset{\sim}{U}(y)\,\underset{\sim}{\mathcal{G}}^{(1)}(y) \;. \tag{V.24b}$$

Because $\underset{\sim}{G}^{(1)}(y)$ is an even function of y (see Eq. (V.20a)) and $\underset{\sim}{G}^{(2)}(y)$ is an odd function of y, it can easily be seen that $\underset{\sim}{\mathcal{G}}^{(1)}(y)$ is even in y and $\underset{\sim}{\mathcal{G}}^{(2)}(y)$ is odd in y. Therefore $\mathcal{G}^{(2)}(y)$ will not contribute to the integral along the imaginary axis because we integrate from $-R$ to R. As a result of the above analysis we can now write the imaginary axis integral as follows:

$$\underset{\sim}{\Gamma}_{axis} = -\frac{1}{\pi}\lim_{R\to\infty}\int_0^R \left[\underset{\sim}{T}(y) + \underset{\sim}{V} + \underset{\sim}{U}(y)(\underset{\sim}{T}(y) + \underset{\sim}{V})^{-1}\underset{\sim}{U}(y)\right]^{-1} dy \,, \tag{V.25}$$

where we have used the fact that $\underset{\sim}{\mathcal{G}}^{(1)}(y)$ is an even function of y. This integral must be evaluated numerically.

To conclude our discussion of the calculation of density matrices using Green's function techniques, let us outline the method for determining the second-order density matrix Γ.

1) We assume that we are given the one-particle Green's function as in Eq. (V.2) as well as a set of basis functions $\left\{\chi_a, a=1,2,\cdots M\right\}$.

2) Form the matrix $\underset{\sim}{B}$ from Eq. (V.17). The contribution to from the arc integral is immediately written:

$$\underset{\sim}{\Gamma}_{arc} = -\frac{1}{2}\underset{\sim}{B} .$$

3) Calculate the matrix $\underset{\sim}{V}$ defined in Eq. (V.12c).

4) Using Eqs. (V.20a) and (V.20b) evaluate $\underset{\sim}{G}^{(1)}(y)$ and $\underset{\sim}{G}^{(2)}(y)$ for any y . This would arise in the numerical evaluation of $\underset{\sim}{\Gamma}_{axis}$.

5) Use Eqs. (V.23) and (V.24) to obtain $\underset{\sim}{\mathscr{G}}^{(1)}(y)$. This too arises in the evaluation of $\underset{\sim}{\Gamma}_{axis}$.

6) Add $\underset{\sim}{\Gamma}_{arc}$ to $\underset{\sim}{\Gamma}_{axis}$ to obtain the resulting $\underset{\sim}{\Gamma}$.

The results of such a calculation will be presented in a paper which will appear in the near future. Hopefully this method will prove useful in calculating second-order density matrices of reasonable accuracy for atomic systems. Certainly it represents a new and interesting method which should be investigated a great deal more in future years.

V. Conclusions

In this paper we have described in considerable detail the application of Green's function techniques to the calculation of the second-order density matrix of an interacting N-particle system. We derived an integral equation for the two-particle Green's function $\mathscr{G}$ which was reduced, after making the random phase approximation, to a matrix equation. We then obtained an expression for the density matrix Γ involving a contour integral of $\mathscr{G}$. Evaluation of this integral was discussed.

In a future paper we will present the results of applying this method to atomic systems. Although such calculations have never before been carried out, we believe that these techniques will prove to be very useful in atomic and molecular problems. The most appealing aspect of Green's functions is that they provide a means of directly calculating reduced quantities without ever having to obtain an N-particle wave function. Certainly this reason alone is sufficient to justify further research.

VI. References

1. W. P. Reinhardt and J. D. Doll, J. Chem. Phys. 50, 2767 (1969).

2. Because of the Fermi statistics, we must have the following equal time commutation relations: $[\psi^+(x,t),\psi(y,t)]_+ = \delta(x-y)$, $[\psi^+(x,t), \psi^+(y,t)]_+ = 0 = [\psi(x,t), \psi(y,t)]_+$, where the symbol $[\,,\,]_+$ means anticommutator.

3. $\Gamma(1,2,1',2') = -\Gamma(2,1,1',2') = -\Gamma(1,2,2',1')$. Similarly for .

4. March, Young, and Sampanthar, The Many-Body Problem in Quantum Mechanics, Cambridge Univ. Press, 1967.

5. Thouless, The Quantum Mechanics of Many-Body Systems, Academic Press (1961).

6. See for example: A. J. Layzer, Phys. Rev. 129, 897 (1963).

7. C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) A191, 39 (1947).