Equation for the direct determination of the density matrix

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A nonvariational equation, called the *density equation*, is proposed for the direct determination of the density matrix *without* using a wave function. It is connected with the Schrödinger equation by a *necessary and sufficient* theorem. The equation for the lowest order depends explicitly only on the fourth-order density matrix $\Gamma^{(4)}$ (or $\Gamma^{(3)}$ in a special case) and not on the higher-order density matrices. The equation always gives the density matrix and the associated energy *which coincide* with those obtained indirectly from the Schrödinger equation. This is true even if we solve the equation only with the known and tractable N-representability conditions, although in such a case some unphysical solution may also occur in the *non-N*-representable space. The equation is applicable to both fermion and boson systems, and to both ground and excited states. In contrast to the Schrödinger equation, the labor of solving the equation does not increase when the number of particles of the system is increased. When we have the Hartree-Fock solution, the equation is transformed such that the correlated density matrix and the correlation energy are the direct solution. *The correlated density equation* thus obtained is suitable for the study of electron correlations.

I. INTRODUCTION

The Schrödinger equation $H\Phi = E\Phi$ and the Pauli principle are the two fundamental principles for the study of stationary electron systems. The Schrödinger equation is a deterministic equation and the Pauli principle gives a constraint for the physically admissible solution. The problem here is that the solution Φ depends on the total N electron coordinates simultaneously and therefore the solution of the Schrödinger equation or its variational variants soon becomes impossible with an increasing number of electrons, N, of the system.

It is well known that all of the physical properties of a system can be evaluated from the second-order density matrix, which is defined by[1]

$$\Gamma^{(2)}(1'2'|12) = {}_NC_2 \int \Phi^*(1', 2', 3, \ldots, N) \times \Phi(1, 2, 3, \ldots, N)\, dx_3 \cdots dx_N .$$

This quantity depends explicitly only on the four electron coordinates and is much simpler mathematically than the wave function itself. Moreover, when we use force[2] instead of energy, all that we need is the electron density $\rho(1)$. This simplifies many of the studies and the underlying concepts of various chemical and physical phenomena.[3,4] Thus it is highly desirable to have a method to determine the density matrix directly without using a wave function. The main difficulty in a variational application of this approach is that the N-representability condition,[5] which is enforced by the Pauli principle, remains unsolved.

The variational principle for $\Gamma^{(2)}$, $E_0 \leq E(\Gamma^{(2)})$, is meaningful only when we have the complete N-representability conditions in a tractable form. So far, the number and complexity of the known N-representability conditions[5-13] are rather discouraging for applications of the variational principle.[8,14] For the electron density $\rho(1)$, the theorem given by Hohenberg and Kohn,[15] $E_0 \leq E(\rho)$, gives a basis for the variational approach.[16] However, the theorem is only an existence theorem and includes an unknown functional.[17] Although we have given previously some explicit operational formulas of this theorem,[18] their exact applications still seem impractical.

The method given in this article does not belong to the variational approach. In Secs. II and III we propose an equation, called the density equation, for the direct determination of the density matrix. The theorem given in Sec. II guarantees that the equation always gives the exact density matrix Γ and the associated energy E which coincide with those obtained indirectly from the Schrödinger equation. This is true even if we do not constrain the complete N-representability conditions simultaneously, although in such a case some unphysical solutions may also occur in the non-N-representable space. Therefore in applications we may use only the tractable N-representability conditions as a constraint, then solve our basic equation, and then select the physically meaningful N-representable solution using the rest of the N-representability criteria. Such a procedure might be more realistic to perform than to first construct completely the N-representable space, which is a prerequisite for the variational approach. Our basic equation includes $\Gamma^{(4)}$ only (or $\Gamma^{(3)}$ in special cases) and not the higher-order density matrices. We hope that it may give a simplification over the N-electron problem of the Schrödinger equation for large N.

In Sec. IV, we transform the density equation such that the exact *correlated* density matrix and the associated correlation energy are obtained as a *direct* solution. Summary and conclusion are given in Sec. V.

II. BASIC THEOREM

In this section we give a theorem which constitutes a basis of the present approach. We imagine an N-electron system such as atomic and molecular systems, but the theorem is general enough for any fermion and boson systems. We suppose here that our density matrix is N representable.

We introduce a symbol $\langle\cdots\rangle_n$,

$$\langle f\rangle_n = \int f(1,\ldots,n,n+1,\ldots,N)\,dx_{n+1}\cdots dx_N\,, \tag{1}$$

which denotes the integration over the last $N-n$ electron coordinates. Since our density matrix is N representable by assumption, we may introduce an antisymmetric wave function $\Psi(1,\ldots,N)$ (assumed to be normalized to unity) such that[19]

$$\Gamma^{(n)} \equiv \Gamma^{(n)}(1'\cdots n'\,|\,1\cdots n) = {}_NC_n\langle\Psi(1',\ldots,n',n+1,\ldots,N),\ \Psi(1,\ldots,n,n+1,\ldots,N)\rangle_n\,, \tag{2}$$

where ${}_NC_n$ is the binomial coefficient and $\Gamma^{(n)}$ is normalized to ${}_NC_n$:

$$\mathrm{Tr}\Gamma^{(n)} \equiv \int \Gamma^{(n)}(1\cdots n\,|\,1\cdots n)\,dx_1\cdots dx_n = {}_NC_n\,. \tag{3}$$

Using $\Psi(1,\ldots,N)$ introduced in Eq. (2), we define the nth-order energy density matrix as

$$G^{(n)} \equiv G^{(n)}(1'\cdots n'\,|\,1\cdots n) = \langle\Psi, H\Psi\rangle_n\,, \tag{4}$$

where H is the Hamiltonian of the system,

$$H = \sum_i^N v(i) + \sum_{i>j}^N w(i,j). \tag{5}$$

The diagonal element of $G^{(n)}$ satisfies

$$\int G^{(n)}(1\cdots n\,|\,1\cdots n)\,dx_1\cdots dx_n = E\,, \tag{6}$$

where E is the energy expectation value of $\Gamma^{(n)}$, which is written alternatively as $E=\langle\Psi, H\Psi\rangle$. Using these quantities, we describe the theorem as follows.

Theorem: A necessary and sufficient condition for Ψ to satisfy the Schrödinger equation,

$$H\Psi = E\Psi, \tag{7}$$

is given by the equality

$$\Gamma^{(n)}(1'\cdots n'\,|\,1\cdots n) = ({}_NC_n/E)G^{(n)}(1'\cdots n'\,|\,1\cdots n) \tag{8}$$

for only a *single* n which is larger than or equal to 2 ($n\geq 2$). We hereafter call Eq. (8) the "density equation."

Proof: Using Eqs. (2) and (4), we can rewrite Eq. (8) as

$$\langle\Psi, (H-E)\Psi\rangle_n = 0. \tag{9}$$

It is trivial that if Ψ satisfies Eq. (7), Eq. (9) holds. We prove the converse. Integrating Eq. (8) or (9) over the last n, $n-1$, and $n-2$ electron coordinates, we obtain

$$E = \langle\Psi, H\Psi\rangle = \int v(1)\Gamma^{(1)}dx_1 + \int w(1,2)\Gamma^{(2)}dx_1dx_2, \tag{10}$$

$$\Gamma^{(1)} = (N/E)G^{(1)}\,, \tag{11}$$

$$\Gamma^{(2)} = ({}_NC_2/E)G^{(2)}\,, \tag{12}$$

respectively. Here we have used abbreviations such as $\int v(1)\Gamma^{(1)}dx_1$ for $\int[v(1)\Gamma^{(1)}(1'|1)]_{1'=1}dx_1$, and will use such abbreviations hereafter. On the other hand, since Ψ and $H\Psi$ have the same symmetry for permutations of coordinates, we have the equality

$$\begin{aligned}\langle\Psi, H^2\Psi\rangle &= \langle\Psi, HH\Psi\rangle \\ &= N\int v(1)G^{(1)}dx_1 + {}_NC_2\int w(1,2)G^{(2)}dx_1dx_2 \\ &= E\left(\int v(1)\Gamma^{(1)}dx_1 + \int w(1,2)\Gamma^{(2)}dx_1dx_2\right) \\ &= E^2.\end{aligned} \tag{13}$$

For the second transformation, we may refer to Eq. (10). We have used the permutation symmetry of the same two particles in Ψ^* and $H\Psi$ in pair.[20] In the third equality, we have used Eqs. (11) and (12). Since the two equalities, $E=\langle\Psi, H\Psi\rangle$ and $E^2=\langle\Psi, H^2\Psi\rangle$, hold if and only if Ψ satisfies $H\Psi = E\Psi$,[21] the theorem is proven. When E is a degenerate level, Ψ is in general a linear combination of the degenerate eigenfunctions of H. Such degenerate states may be discriminated further by imposing other symmetry requirements on Γ (e.g., space symmetry, orbital and spin angular momentum symmetries, etc.).

Because the theorem is a necessary and sufficient theorem, we may use the density equation (8) as our basic equation instead of the Schrödinger equation (7). The theorem guarantees that *every* density equation for $n\geq 2$ is a deterministic equation in the N-representable space. However, at this stage, the energy density matrix appearing in the density equation is defined by Eq. (4) using the wave function Ψ. For our purpose (mentioned in Sec. I) we have to eliminate this Ψ from our expression and obtain the density equation in the

form which includes only the density matrix as a variable. The theorem suggests that the resultant equation may be used for determining the density matrix directly without using indirectly the Schrödinger equation for Ψ.

Before performing the above transformation, we want to say a few words about the theorem. A literal meaning of the density equation is that in order that the density matrix be exact, it must be everywhere proportional locally to the energy density matrix with the proportionality constant ${}_NC_n/E$. In the theorem, the first-order density equation

$$\rho(1'|1)=(N/E)g(1'|1), \tag{14}$$

where $\rho(1'|1)=\Gamma^{(1)}(1'|1)$ and $g(1'|1)=G^{(1)}(1'|1)$, is missing. This is because our Hamiltonian includes up to two-particle interaction terms [Eq. (5)]. It is evident, however, that the first-order density equation gives a necessary condition, but for sufficiency we need an assumption discussed in Sec. III B. When $n=N$, the theorem is trivial. The Nth-order density equation, which is written as $\Psi^*\Psi=\Psi^*H\Psi/E$, is just the Schrödinger equation, since Ψ is nonzero.

III. DENSITY EQUATION

In this section we rewrite the density equation in the form which includes only the density matrix as a variable, and we consider a method to use the resultant equation for the direct determination of the density matrix.

For the time being, we again assume that our density matrix is N representable, i.e., we assume the existence of $\Psi(1,\ldots,N)$, as defined by Eq. (2). Then the energy density matrix $G^{(n)}$ defined by Eq. (4) can be transformed as

$$G^{(n)}={}_NC_n)^{-1}\Big[\Big(\sum_i^n v(i)+\sum_{i>j}^n w(i,j)\Big)\Gamma^{(n)}+(n+1)\int\Big(v(n+1)+\sum_i^n w(i,n+1)\Big)\Gamma^{(n+1)}dx_{n+1}$$
$$+\frac{(n+1)(n+2)}{2}\int w(n+1,n+2)\Gamma^{(n+2)}dx_{n+1}dx_{n+2}\Big], \tag{15}$$

where the operators v and w are defined in Eq. (5). Here we note again the abbreviations such as $\int v(n+1)\Gamma^{(n+1)}dx_{n+1}$ for

$$\int[v(n+1)\Gamma^{(n+1)}(1'\cdots n'(n+1)'|1\cdots n(n+1))]_{(n+1)'=n+1}dx_{n+1}.$$

In the transformation (15), we have used the permutation symmetry of the same two particles in Ψ^* and Ψ in pair. This point will be used later when we expand our space somewhat from the N-representable space. Inserting this expression into Eq. (8), our density equation becomes

$$E\Gamma^{(n)}=\Big(\sum_i^n v(i)+\sum_{i>j}^n w(i,j)\Big)\Gamma^{(n)}+(n+1)\int\Big(v(n+1)+\sum_i^n w(i,n+1)\Big)\Gamma^{(n+1)}dx_{n+1}$$
$$+\frac{(n+1)(n+2)}{2}\int w(n+1,n+2)\Gamma^{(n+2)}dx_{n+1}dx_{n+2}. \tag{16}$$

In this form, the density equation includes the density matrices from order n to $n+2$. It coincides with one of the coupled chain of equations in a density matrix form of the equations for the Green's functions.[22] However, it is incorrect to regard Eq. (16) as only one element of such chain of equations, since the theorem given in Sec. II shows that for $n\geq 2$, *every* density equation is equivalent with the Schrödinger equation when our Γ is N representable. This point is realized more explicitly in our formalism by considering $\Gamma^{(n+2)}$ as our basic variable instead of $\Gamma^{(n)}$, since we have the following recurrence formula for our density matrix:

$$\int\Gamma^{(p)}(1'\cdots(p-1)'p|1\cdots(p-1)p)dx_p$$
$$=\frac{N-p+1}{p}\Gamma^{(p-1)}(1'\cdots(p-1)'|1\cdots(p-1)). \tag{17}$$

Stressing this point explicitly, we rewrite Eq. (16) in an alternative form

$$\int[\mathcal{H}^{(n)}(1\cdots n;(n+1)(n+2))-E]\Gamma^{(n+2)}dx_{n+1}dx_{n+2}=0, \tag{18}$$

where $\mathcal{H}^{(n)}$ is a *reduced* Hamiltonian defined by

$$\mathcal{H}^{(n)}(1\cdots n;(n+1)(n+2))=\sum_i^n v(i)+\sum_{i>j}^n w(i,j)+(N-n)\Big(v(n+1)+\sum_i^n w(i,n+1)\Big)+\frac{(N-n)(N-n-1)}{2}w(n+1,n+2). \tag{19}$$

Thus the density equation is given in a *closed* form in which only $\Gamma^{(n+2)}$ is a variable. The previous theorem shows that we may use the density equation (16) or (18) as our deterministic equation for $\Gamma^{(n+2)}$ *instead* of the Schrödinger equation for Ψ. Evidently, the density equation is valid for both fermion and boson systems.

In the reduced Hamiltonian $\mathcal{H}^{(n)}$, the first two terms are the direct terms due to the first n electrons. The last two terms are the contributions of the last $N-n$ electrons represented by the two electrons, $n+1$ and $n+2$, chosen arbitrarily from the last $N-n$ electrons. Then $\mathcal{H}^{(n)}(1\cdots n;(n+1)(n+2))$ is symmetric for the first n electrons and can be made symmetric for the representative electrons $n+1$ and $n+2$, but it is not symmetric for the interchange between the first n electrons and the two electrons $n+1$ and $n+2$.

Practically, our interest may lie only in the density equation of lower order. When $n=1$, we obtain the first-order density equation, but since it gives only a necessary condition for the hidden Ψ to satisfy the Schrödinger equation, we postpone the discussion to a later section. The necessary and sufficient condition is first realized when $n=2$, for which Eq. (18) becomes

$$\int [\mathcal{H}^{(2)}(12;34)-E]\,\Gamma^{(4)}(1'2'3'4'|1234)\,dx_3\,dx_4=0, \tag{20}$$

where

$$\begin{aligned}\mathcal{H}^{(2)}(12;34) &= v(1)+v(2)+w(1,2)\\ &\quad +(N-2)[v(3)+w(1,3)+w(2,3)]\\ &\quad +\tfrac{1}{2}(N-2)(N-3)w(3,4)\,. \end{aligned}\tag{21}$$

Here, the variable is $\Gamma^{(4)}$ only, which depends explicitly on eight electron coordinates. When the two-electron operator w does not include the differential operator, we can replace

$$\Gamma^{(4)}(1'2'3'4'|1234)$$

in Eq. (20) with

$$\Gamma^{(4)}(1'2'3'4|1234),$$

and then the problem becomes a seven-electron problem. When we obtain $\Gamma^{(4)}$ by solving Eq. (20), we can calculate any observable quantity of the system from it. Therefore the N-particle Schrödinger equation may be replaced with the second-order density equation, since these two equations are connected by the necessary and sufficient theorem. The total number of electrons of the system, N, is included in our density equation only as a constant factor in the reduced Hamiltonian $\mathcal{H}^{(n)}$. Therefore the labor of solving the density equation does *not* increase with an increased number of electrons of the system. This merit, which is common to the density approach, is in marked contrast with the wave-function approach, in which an increase in N causes a tremendous increase in difficulty of solution. Although the solution of the density equation itself might be difficult, we hope that it may still be a simplification over the N-electron problem of the Schrödinger equation.

In comparison with the variational principle for Γ, $E_0 \leq E(\Gamma^{(2)})$, the density equation includes $\Gamma^{(4)}$ explicitly. (As described later, it is reduced to $\Gamma^{(3)}$ in the first-order density equation.) However, as discussed below, the density equation does not necessarily require the complete N-representability condition as a prerequisite for application. Moreover, it would be applicable to an excited state as well as a ground state. This is evident from the proof of the previous theorem.

A. N representability

So far, we have assumed that our density matrix is N representable. When the density matrix is N representable, three expressions of the density equation, Eqs. (8), (16), and (18), are equivalent, and the theorem given in Sec. II holds for each of them. Then, we know that the density equation (16) or (18) must give a unique[23] exact solution (the density matrix $\Gamma^{(n+2)}$ and the associated energy) in the N-representable space of Γ. This is true even if we solve our density equation in the wider space than the N-representable space, since the equation is a nonvariational equation. When we constrain our space by the *complete* N-representability conditions, if known, *every* solution must be identical with the one obtained indirectly by solving the Schrödinger equation.[23] On the other hand, when we use only the known and tractable N-representability conditions, the solutions may possibly include unphysical ones which do *not* lie in the N-representable space, but at the same time, we know that the solutions *must* include the correct exact one which is always in the N-representable space. The rest of the N-representability conditions are utilized in order to select the correct solution. When we have the experimental values for some properties of the system of interest, they may be used as subcriteria, since we don't know the complete N-representability condition.

At present, only the latter procedure is realistic. Moreover, it might be more practical than the former, considering the complexity of the known N-representability conditions.[5-13] Many of the known N-representability conditions, e.g. those

given as inequalities, seem to be more easily used as the criteria of the N representability of a *given* density matrix rather than as the constraints for the functional space to which the solutions must belong. For the variational approach based on $E_0 \leq E(\Gamma^{(2)})$, the knowledge of the complete N-representability condition is required. Therefore at present its application is impossible in an exact sense. Adding to the difficulty in obtaining the complete N-representability conditions, the number and complexity of the conditions known so far are rather discouraging for applications of the variational principle.

Some of the well-known necessary conditions[7(a)] for the N-representability are that (a) Γ must be Hermitian, (b) Γ must have a finite trace [Eq. (3)], (c) Γ must be antisymmetric (for fermions), (d) Γ must be positive semidefinite, and (e) Γ must satisfy

$$\int \Phi(1', \ldots, p')\Gamma^{(p)}(1' \cdots p' | 1 \cdots p) \times \Phi^*(1, \ldots, p)\, dx_1 \cdots dx_p'\, dx_1 \cdots dx_p \leq 1, \quad (22)$$

for any normalized Slater determinant Φ of p electrons. For the density equation, an appropriate choice of the conditions used as constraints will serve to reduce unphysical solutions. Especially conditions (a) and (b) are important in order to make the equation meaningful. Condition (c) is also quite tractable. A merit of imposing condition (d) will be seen below. Condition (e) will be discussed later in connection with the equation for the correlated density matrix.

Since the density equation itself is a strong restriction for the physically admissible solution, it works, to some extent, to restrict its solution in the N-representable space. This is similar to, and stems from, the fact that the solution Ψ of the Schrödinger equation $H\Psi = E\Psi$ always belongs to the symmetric or antisymmetric space and the mixed symmetry does not arise. For the density approach, such *automatic* selection of the space of the solution is very valuable.

For instance, we expand our space somewhat from the N-representable space. We assume that (i) we can write our density matrix as

$$\Gamma^{(n)}(1' \cdots n' | 1 \cdots n) = {}_N C_n \int \tilde{\Psi}^*(1', \ldots, n', n+1, \ldots, N) \times \tilde{\Psi}(1, \ldots, n, n+1, \ldots, N)\, dx_{n+1} \cdots dx_N, \quad (23)$$

and (ii) the symmetries of $\tilde{\Psi}$ for permutations between the first n and the last $N-n$ coordinates and among the last $N-n$ coordinates are completely symmetric, completely antisymmetric, and mixed ones of both. For the first n coordinates, we may require the antisymmetric condition (c). We note that assumption (i) is realized when we impose the Hermitian and positive semidefinite conditions (a) and (d). Let $\{\phi_i\}$ be a complete orthonormal set for the n-electron space; then our $\Gamma^{(n)}$ is expanded as

$$\Gamma^{(n)}(1' \cdots n' | 1 \cdots n) = \sum_{i,j} d_{ij}\, \phi_i^*(1', \ldots, n')\phi_j(1, \ldots, n). \quad (24)$$

Since the matrix $\underline{d}$ is Hermitian and positive semidefinite,[24] we may assume the existence of a set of functions $\{\chi_i\}$ which satisfies[25]

$$d_{ij} = \int \chi_i^*(n+1, \ldots, N)\chi_j(n+1, \ldots, N)\, dx_{n+1} \cdots dx_N. \quad (25)$$

With these functions $\{\chi_i\}$, we can define $\tilde{\Psi}$ as

$$\tilde{\Psi}(1, \ldots, n, n+1, \ldots, N) = \sum_i \phi_i(1, \ldots, n)\chi_i(n+1, \ldots, N), \quad (26)$$

which satisfies Eq. (23). Thus assumption (i) is realized as a result of conditions (a) and (d). The recurrence formula (17) also follows immediately from Eq. (23). Assumption (ii) restricts somewhat the symmetry of $\tilde{\Psi}$. It was imposed in order to assure the transformation of $\tilde{G}^{(n)} \equiv \langle \tilde{\Psi}, H\tilde{\Psi} \rangle_n$ as given by Eq. (15).

Even in this expanded space of Γ, the three expressions of the density equation, Eqs. (8), (16), and (18), are equivalent and the previous theorem also holds, as seen from the proof.[20] Therefore the solution Γ and E of the density equation in this expanded space should also be identical with the one obtained indirectly from the Schrödinger equation, i.e., $\tilde{\Psi}$ should satisfy $H\tilde{\Psi} = E\tilde{\Psi}$, which is possible only when $\tilde{\Psi}(1, \ldots, n, n+1, \ldots, N)$ is antisymmetric for *all* permutations of N electrons. Thus even in this expanded space the exact N-representable solution is the *only* solution of the density equation, and no unphysical solutions accompany it. In general, such automatic selection of the space of the solution is very interesting.

B. First-order density equation

The first-order density equation given by Eq. (14) is a necessary condition for the *hidden* Ψ to satisfy the Schrödinger equation. This means that at least one solution in the N-representable space is the exact one. Inserting $n=1$ into Eqs. (16) and (18), we obtain alternative expressions of the first-order density equation. They are

$$E\rho = v(1)\rho + 2\int [v(2)+w(1,2)]\,\Gamma^{(2)}dx_2 + 3\int w(2,3)\Gamma^{(3)}dx_2\,dx_3, \tag{27}$$

and

$$\int [\mathcal{H}^{(1)}(1;23) - E]\,\Gamma^{(3)}(1'2'3'|123)\,dx_2\,dx_3 = 0, \tag{28}$$

where the reduced Hamiltonian $\mathcal{H}^{(1)}$ is given by

$$\mathcal{H}^{(1)}(1;23) = v(1) + (N-1)[v(2)+w(1,2)] + \tfrac{1}{2}(N-1)(N-2)w(2,3)\,. \tag{29}$$

As seen in these expressions, the unknown variable is $\Gamma^{(3)}$, which depends explicitly on the six electron coordinates. When w does not include a differential operator, the problem is reduced to a five-electron problem. In comparison with the previous second-order equation, the order of the variable is reduced here from $\Gamma^{(4)}$ to $\Gamma^{(3)}$. Since this simplification would be very useful in practical applications, it is worthwhile to consider the condition under which the first-order density equation can also become a sufficient condition for the hidden Ψ to satisfy $H\Psi = E\Psi$.

It is evident from the proof of the previous theorem that if the Hamiltonian of the system does not include the two-particle operator $w(i,j)$, the first-order density equation is also a sufficient condition for $H\Psi = E\Psi$. The same is true for such a *model* Hamiltonian, and in this case Ψ is the wave function of the model system (e.g., the Hartree-Fock model discussed in Sec. III C). For two-particle systems (where we have at most $\Gamma^{(2)}$), a condition for the sufficiency is that the natural orbitals of ρ having nonzero eigenvalues form a complete set. The proof is given in the Appendix. This condition might not be unrealistic, since for wave functions containing interparticle coordinate r_{12} explicitly, the rank of ρ, defined as the number of nonzero eigenvalues, is infinite.[26] In general, when we define the N-electron function Φ by $\Phi \equiv (H-E)\Psi$ in Eq. (9), the first-order density equation requires that the transition density between Ψ and Φ, $\rho_{\Psi\Phi}(1'|1)$, be zero identically, or Ψ and Φ be strongly orthogonal. If such Φ can not exist except for $\Phi = 0$ (i.e., $H\Psi = E\Psi$), the first-order density equation becomes also the sufficient condition. The above condition imposed for the two-particle systems guarantees such a situation (see the Appendix).

Considering the stringency of the restriction set by the first-order density equation, we believe that even in general case the equation would be close to the sufficient condition. Moreover, since we know from the necessity that at least *one* solution in the N-representable space is the exact solution, we may use the first-order density equation for the direct determination of the density matrix $\Gamma^{(3)}$. Finally, the first-order density equation has properties common to the general cases studied in the previous sections.

C. Approximate solution and the Hartree-Fock model

We next consider an approximate solution of the density equation. Since the density matrix has a probabilistic interpretation, we may approximate the higher-order density matrices appearing in the last two terms of Eq. (16) by the products of the lower-order density matrices. When we introduce such a decoupling approximation, the density equation (16) is simplified to an equation for the nth-order density matrix, since we have the recurrence formula (17). In such a decoupling approximation, which is commonly adopted in many-body theories[27] such as the Green's-function technique,[22,28] a caution is necessary for the N representability.

In this respect, the first-order density equation studied in Sec. III B may be used as a basic equation for the one-particle approximation. Actually, as may be expected from the result of the Green's-function method,[22] the decoupling approximation of the higher-order density matrices, $\Gamma^{(2)}$ and $\Gamma^{(3)}$ in Eq. (27), by the single-determinantal ones leads to the Hartree-Fock (HF) equation. In this approximation, the N representability of the density matrix is satisfied automatically.[1]

We approximate $\Gamma^{(2)}$ and $\Gamma^{(3)}$ in Eq. (27) by

$$\Gamma^{(p)} \simeq \Gamma_0^{(p)} \equiv (1/p!)\det\{\rho_0(1'|1), \rho_0(2'|2), \ldots, \rho_0(p'|p)\}, \tag{30}$$

and ρ by

$$\rho(1'|1) \simeq \rho_0(1'|1) \equiv \sum_i^N \varphi_i^*(1')\varphi_i(1)\,, \tag{31}$$

where $\{\varphi_i\}$ $(i = 1, \ldots, N)$ is an orthonormal set of occupied orbitals. Then the first-order density equation becomes, after manipulation,

$$h(1)\rho_0(1'|1) = \sum_{i,j}^N \epsilon_{ji}\varphi_i^*(1')\varphi_j(1)\,, \tag{32}$$

where $h(1)$ and ϵ_{ji} are the familiar single-electron operator and its matrix element,

$$h(1) = v(1) + \sum_k^N [J_k(1) - K_k(1)], \quad \epsilon_{ji} = \langle \varphi_j, h\varphi_i \rangle. \tag{33}$$

Using Eq. (31), we can rewrite Eq. (32) as

$$h(1)\varphi_i(1) = \sum_j^N \epsilon_{ji}\varphi_j(1)\,, \tag{34a}$$

which is the Euler equation for the HF theory. Since ρ_0 is independent of unitary transformations among the occupied orbitals, we can choose the unitary transformation such that $\epsilon_{ji}=\epsilon_i\delta_{ji}$. We then have the standard form of the HF equation,

$$h(1)\varphi_i(1)=\epsilon_i\varphi_i(1). \tag{34b}$$

When we add to both sides of Eq. (34a) a Hermitian identity and then diagonalize, we have the modified form of the HF equation.[29,30] Thus we could obtain the HF equation as an approximation to the first-order density equation.

The HF theory may be viewed from different aspects. First, it is a theory for a model system defined by the Hamiltonian $H_0=\sum_i^N h(i)$. Since H_0 is the sum of the single-electron operators, the first-order density equation constitutes a necessary and sufficient condition for the exact density matrix of the *model* system. A complete N-representability condition for the system is given by Eqs. (30) and (31).[1] Dropping the operator w in Eq. (27), replacing v with h, and imposing the N-representability condition, we can easily verify that the HF equation [(32) or (34)] is just the first-order density equation for the model system in the N-representable space. Evidently, the solution is identical with the one obtained from the Schrödinger equation $H_0\Psi_0=E_0\Psi_0$ for the model system, where Ψ_0 is the HF single-determinantal wave function and E_0 the HF energy given by

$$E_0=\langle\Psi_0, H_0\Psi_0\rangle=\int h(1)\rho\, dx_1.$$

Second, in the studies of electron correlation, the HF model is often used as a convenient starting point.[27] In the present density equation approach, it would be convenient to write the HF equation as

$$\langle\Psi_0, (H_0-E_0)\Psi_0\rangle_n=0, \tag{35a}$$

which is written alternatively from Eq. (16) as

$$E_0\Gamma_0^{(n)}=\left(\sum_i^n h(i)\right)\Gamma_0^{(n)}+(n+1)\int h(n+1)\Gamma_0^{(n+1)}dx_{n+1}. \tag{35b}$$

In Sec. IV, we consider an equation which gives the correlation correction to the density matrix as a direct solution. In the perturbation theory, Eq. (35) constitutes a zeroth-order equation for the perturbation expansion.

IV. CORRELATED DENSITY EQUATION

When we have the Hartree-Fock solution or when we want to study only the correlation effects, it is sometimes more convenient to transform beforehand our basic equation such that the correlation correction is the direct solution.

For this purpose, we define the "correlated density matrix" $C^{(p)}$ by

$$\Gamma^{(p)}(1'\cdots p'|1\cdots p)=\Gamma_0^{(p)}(1'\cdots p'|1\cdots p)+C^{(p)}(1'\cdots p'|1\cdots p), \tag{36}$$

where $\Gamma_0^{(p)}$ is the HF density matrix defined by Eq. (30). The correlated density matrix $C^{(p)}$ includes the correlation correction to all orders in the perturbation theoretic treatment. Since $\Gamma_0^{(p)}$ satisfies the same normalization condition and recurrence formula as those of the total density matrix $\Gamma^{(p)}$ [Eqs. (3) and (17)], the correlated density matrix satisfies

$$\mathrm{Tr}C^{(p)}=\int C^{(p)}(1\cdots p|1\cdots p)dx_1\cdots dx_p=0 \tag{37}$$

and

$$\int C^{(p)}(1'\cdots(p-1)'p|1\cdots(p-1)p)\,dx_p=\frac{N-p+1}{p}C^{(p-1)}(1'\cdots(p-1)'|1\cdots(p-1)). \tag{38}$$

Other N-representability conditions for Γ may also be transformed to those for the correlated density matrix C. Inserting Eq. (36) into the density equation [Eq. (16) or (18)] and simplifying the result using the HF equation, we obtain the equation for the correlated density matrix C. From the theorem given in Sec. II, the resultant equation, which we call the correlated density equation, is a deterministic equation which gives *directly* the exact correlated density matrix and the associated correlation energy in the "N-representable" space of C.

Practically, our interest may lie only in the lower-order equation. For $n=2$, the above procedure gives the second-order correlated density equation as

$$\int[\mathcal{K}^{(2)}(12;34)-E]C^{(4)}dx_3dx_4+\frac{1}{12}(N-2)(N-3)\Big([w(1,2)-E^{\mathrm{corr}}]\Gamma_0^{(2)}(12|12)-\int w(1,3)\Gamma_0^{(2)}(12|13)\rho_0(3|2)dx_3-\int w(2,3)\Gamma_0^{(2)}(21|23)\rho_0(3|1)dx_3+\int w(3,4)\Gamma_0^{(2)}(12|34)\Gamma_0^{(2)}(34|12)dx_3dx_4\Big)=0, \tag{39}$$

where $\mathcal{H}^{(2)}(12;34)$ is the reduced Hamiltonian given by Eq. (21) and E^{corr} is the correlation energy,

$$E^{\mathrm{corr}} = E - E_{\mathrm{HF}}, \tag{40}$$

where E_{III} is the HF energy expectation value,

$$E_{\mathrm{III}} = \int v(1)\rho_0(1'|1)\,dx_1 + \int w(1,2)\Gamma_0^{(2)}(12|12)\,dx_1\,dx_2\,, \tag{41}$$

which is different from the previous E_0 in the electron repulsion part. In the correlated density equation (39), the correlated density matrix $C^{(4)}$ in the first term and the associated correlation energy E^{corr} are the ones to be solved. The terms in the large parentheses depend only on the HF density matrices, which are (assumed to be) known. They represent the field due to the HF densities.

Using the recurrence formula (38), the correlated density equation (39) is written alternatively as

$$[v(1)+v(2)+w(1,2)-E]C^{(2)}+[w(1,2)-E^{\mathrm{corr}}]\Gamma_0^{(2)}(12|12)+3\int v(3)C^{(3)}dx_3+\int w(1,3)[3C^{(3)}-\Gamma_0^{(2)}(12|13)\rho_0(3|2)]\,dx_3$$
$$+\int w(2,3)[3C^{(3)}-\Gamma_0^{(2)}(21|23)\rho_0(3|1)]\,dx_3+\int w(3,4)[6C^{(4)}+\Gamma_0^{(2)}(12|34)\Gamma_0^{(2)}(34|12)]\,dx_3\,dx_4=0. \tag{42}$$

This expression corresponds to Eq. (16) as the expression (39) does to Eq. (18). As in Sec. III C, this form of the correlated density equation would be suitable for approximate solution. When we introduce a decoupling approximation for the higher-order correlated density matrices $C^{(3)}$ and $C^{(4)}$, Eq. (42) is simplified to an equation which includes only $C^{(2)}$ as a variable. Since the physics for the correlated density matrix may be different from that for the total density matrix, the decoupling approximation for the correlated density equation may be different from that for the density equation.

The first-order density equation also gives the correlated density equation via a similar procedure. The resultant equation is a necessary condition that the exact correlated density matrix must satisfy. It is given by

$$\int[\mathcal{H}^{(1)}(1;23)-E]C^{(3)}dx_2\,dx_3=\tfrac{1}{6}(N-1)(N-2)E^{\mathrm{corr}}\rho_0\,, \tag{43}$$

corresponding to Eq. (37), and by

$$[v(1)-E]C^{(1)}+2\int[v(2)+w(1,2)]C^{(2)}dx_2$$
$$+3\int w(2,3)C^{(3)}dx_2\,dx_3=E^{\mathrm{corr}}\rho_0\,, \tag{44}$$

corresponding to Eq. (42). The reduced Hamiltonian $\mathcal{H}^{(1)}(1;23)$ in Eq. (43) is given by Eq. (29). In comparison with the second-order equations (39) and (42), these first-order correlated density equations have *much* simpler forms, and the variable is only $C^{(3)}$ instead of $C^{(4)}$.

Some interesting properties of the correlated density matrix C are derived from those of the total density matrix Γ. From the N-representability conditions (d) and (e), we obtain the following conditions for $C^{(p)}$: We define ${}_NC_p$ p-particle single determinants

$$\phi_I(1,\ldots,p)=(p!)^{-1/2}\det\{i_1(1),i_2(2),\ldots,i_p(p)\} \tag{45}$$

composed of the occupied HF orbitals $i=\varphi_i$ given by Eq. (34). I denotes a set of integers, $i_1<i_2<\cdots<i_p$. Using these single determinants, we rewrite the HF density matrix $\Gamma_0^{(p)}$ of Eq. (30) as[1]

$$\Gamma_0^{(p)}(1'\cdots p'|1\cdots p)=\sum_{I=1}^{{}_NC_p}\phi_I^*(1',\ldots,p')\phi_I(1,\ldots,p)\,, \tag{46}$$

which is a generalization of Eq. (31). From Eqs. (22), (36), and (46), conditions (d) and (e) give the following condition for $C^{(p)}$:

$$-1\leq\langle\phi_I|C^{(p)}\phi_I^*\rangle\leq 0, \tag{47}$$

where

$$\langle\phi_I|C^{(p)}\phi_I^*\rangle=\int\phi_I(1',\ldots,p')C^{(p)}(1'\cdots p'|1\cdots p)$$
$$\times\phi_I^*(1,\ldots,p)\,dx_1'\cdots dx_p'\,dx_1\cdots dx_p.$$

The left-hand-side inequality is due to the positive semidefinite condition (d). Similarly, for the p-particle single determinant ϕ_K which is orthogonal to all of the ϕ_I ($I=1,\ldots,{}_NC_p$), given by Eq. (45), we obtain

$$0\leq\langle\phi_K|C^{(p)}\phi_K^*\rangle\leq 1. \tag{48}$$

Such $\phi_K(1,\ldots,p)$ are constructed from Eq. (45) by replacing one, two, etc, occupied orbitals with the unoccupied orbitals. The sum of the sets $\{\phi_I\}$ and $\{\phi_K\}$ forms an orthonormal complete set.

Since the correlated density matrix C is Hermitian, we can define the functions $\{\eta_i\}$, which diagonalize C, as

$$C^{(p)}(1'\cdots p'|1\cdots p)=\sum_i\mu_i\eta_i^*(1',\ldots,p')\eta_i(1,\ldots,p). \tag{49}$$

The functions $\{\eta_i\}$ may be called "natural correlated p functions." They form an orthonormal set (complete if we include functions belonging to eigenvalue zero). The eigenvalues μ_i may be positive, negative, or zero ($\mu_1 \leq \mu_2 \leq \cdots \leq 0 \cdots \leq \mu_i \leq \cdots$), but the sum satisfies

$$\sum_i \mu_i = 0 , \tag{50}$$

from Eq. (37). From Eqs. (47) and (48), we obtain the inequalities which the natural correlated p functions should satisfy. They are

$$-1 \leq \sum_i \mu_i |\langle \phi_I, \eta_i \rangle|^2 \leq 0, \quad I = 1, \ldots, {}_N C_p , \tag{51}$$

$$0 \leq \sum_i \mu_i |\langle \phi_K, \eta_i \rangle|^2 \leq 1, \quad K = {}_N C_p + 1, \ldots, \infty . \tag{52}$$

Since $|\langle \phi_I, \eta_i \rangle|^2$ is positive, the inequality (51) suggests that the natural correlated p functions having *negative* eigenvalues would have large overlap with the HF (occupied) p functions ϕ_I. When $p = 1$, the functions $\eta_i(1)$ may be called natural correlated orbitals, and the HF functions ϕ_I and ϕ_K are simply the HF occupied orbitals φ_i and φ_k, respectively. By a similar argument, we expect from Eq. (51) that the natural correlated orbitals having negative eigenvalues would have large overlap with and therefore resemble the HF occupied orbitals φ_i or their proper unitary transformation. These properties of the natural correlated functions may be of value for the description of the correlation effects. Inserting Eq. (49) into our correlated density equation [e.g., Eqs. (39) or (42)], we can derive the equation which determines the natural correlated p functions and orbitals.

V. SUMMARY AND CONCLUSION

In this paper, a nonvariational equation is proposed for the *direct* determination of the density matrix without using wave functions. The equation, called the density equation, is connected with the Schrödinger equation by the *necessary and sufficient* theorem. It gives the density matrix and the associated energy which *coincide* with those obtained indirectly from the Schrödinger equation. The equation may therefore be considered as giving a *projection* of the Schrödinger equation onto the fewer-particle space. The equation for the lowest order depends explicitly only on the fourth-order density matrix $\Gamma^{(4)}$ (or $\Gamma^{(3)}$ in the special case) and not on the higher-order density matrices. The equation is applicable to both fermion and boson systems and to both ground and excited states. In contrast with the Schrödinger equation, the labor of solving the equation does not increase with increased number of particles of the system. We hope that the density equation may give a simplified procedure dealing with N-electron systems to which the Schrödinger equation is difficult to apply.

When we impose simultaneously the complete N-representability condition, if known, every solution of the density equation must be exact, i.e., identical with the one obtained indirectly from the Schrödinger equation. Even if we impose only incomplete and tractable N-representability conditions, as is possible at present, the equation gives a unique exact solution in the N-representable space,[23] although it may possibly give, at the same time, some unphysical solutions in the non-N-representable space. The rest of the N-representability conditions may be used for selecting the correct solution. Moreover, the density equation works, to some extent, to restrict its solution in the N-representable space. Thus we can expand our space somewhat from the N-representable space without getting unphysical solutions. These properties of the density equation would be useful in comparison with the variational principle for Γ, $E_0 \leq E(\Gamma^{(2)})$.

When we have the Hartree-Fock solution, which is an approximate solution of the first-order density equation, the density equation is transformed so that the correlated density matrix and the correlation energy are the direct solution. The correlated density equation thus obtained is suitable for the study of electron correlation. The natural correlated functions and orbitals which diagonalize the correlated density matrices have properties which may be of value for the description of the correlation effects.

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APPENDIX

Here we show that the first-order density equation for two-particle systems is also a sufficient conditon for the hidden Ψ to satisfy the Schrödinger equation, if the natural orbitals χ_i of ρ having nonzero eigenvalues form a complete set in the one-particle space.

Using the expansion theorem of Carlson and Keller,[31] the wave function in Eq. (9) for $n = 1$ is

expressed as

$$\Psi(12)=\frac{1}{\sqrt{2}}\sum_{i}^{\infty}\lambda_i\chi_i(1)\zeta_i(2)\,, \tag{A1}$$

where λ_i^2 is equal to the occupation number of χ_i. By assumption, $\lambda_i\neq 0$ for any i which runs to infinity [the rank of $\rho(1'|1)$ is infinite]. The dual functions ζ_i are in general the natural functions of $\Gamma^{(N-1)}$ and they correspond to the different choice of the natural orbitals in the two-particle case.[26] As given by Smith,[7(b)] the N representable $\rho(1'|1)$ of an even-N-electron system has at least twofold degenerate eigenvalues. Thus by assumption *both* $\chi_i(1)$ and $\zeta_i(2)$ form complete sets, and we can expand $(H-E)\Psi$ as

$$\Phi(12)\equiv(H-E)\Psi=\sum_{j,k}a_{jk}\chi_j(1)\zeta_k(2)\,. \tag{A2}$$

Inserting Eqs. (A1) and (A2) into Eq. (9) for $n=1$, we obtain

$$\langle\Psi,(H-E)\Psi\rangle_1=\frac{1}{\sqrt{2}}\sum_{i,j}\lambda_i a_{ji}\chi_i^*(1')\chi_j(1)=0. \tag{A3}$$

Since $\{\chi_i(1)\}$ is linearly independent, the product $\{\chi_i^*(1')\chi_j(1)\}$ is also linearly independent. Then Eq. (A3) gives $\lambda_i a_{ji}=0$ for any i and j. Since all λ_i are nonzero, by assumption, we obtain $a_{ji}=0$ for any i and j. Therefore Eq. (A2) becomes $(H-E)\Psi=0$, which proves the sufficiency.[32] The necessity is evident from Eq. (9).

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[20] This suggests that the theorem holds for a wider space of N-coordinate functions than the purely antisymmetric Ψ space. This point will be used later when we expand our Γ space somewhat from the N-representable space.

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[25] See Theorem 1 in Ref. 8.

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