

Regular article

Equation for the direct determination of the density matrix: Time-dependent density equation and perturbation theory*

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Abstract. The density equation proposed previously for the direct determination of the density matrix, i.e. for the wave mechanics without wave, is extended to a time-dependent case. The time-dependent density equation has been shown to be equivalent to the time-dependent Schrödinger equation so long as the density matrix, included as a self-contained variable, is N -representable. Formally, it is obtainable from the previous time-independent equation by replacing the energy E with $i\hbar \frac{\partial}{\partial t}$. The perturbation theory formulas for the density equation have also been given for both the time-dependent and time-independent cases.

Key words: Density equation – Time-dependent density equation – Perturbation theory

1 Introduction

The non-relativistic electronic state is determined by the Schrödinger equation constrained by the Pauli exclusion principle. We restrict ourselves, for a while, to fermions but the argument is also valid for bosons. The Schrödinger equation is an equation of motion of the wave function which depends on all the N -electron coordinates, where N is the number of the electrons of the system, and the Pauli exclusion principle is an antisymmetric condition for the exchange of any two electrons of the system. On the other hand, all the elementary observables in quantum mechanics are composed of one- and/or two-electron operators, so that all such quantities are calculated only with the knowledge of the second-order density matrix (2-DM) defined by [1]

$$\Gamma^{(2)}(1'2'|12) = {}_N C_2 \int \Psi^*(1'2'3 \dots N) \Psi(123 \dots N) dx_3 \dots dx_N . \quad (1)$$

The 2-DM depends only on the four coordinates, while the wave function depends on the N -coordinates. Therefore, it would be a great simplification if we could find the equation-of-motion of the 2-DM itself.

Such an equation-of-motion was derived by the present author in 1976 as the density equation [2], which is connected with the Schrödinger equation by the necessary and sufficient conditions. The Pauli condition in the wave function space becomes the N -representability condition [3] for the density matrix. Figure 1 shows the relation between these two methods. A problem in the density equation method is that the N -representability condition is not yet completely known, despite the efforts of many researchers [4]. The Pauli (exclusion) principle is trivial in the wave function space so that we still use the wave function approach despite the simplicity of the 2-DM.

Let us define the Hamiltonian of the system by

$$H(1 \dots N) = \sum_i v(i) + \sum_{i>j} w(i, j) , \quad (2)$$

where $v(i)$ and $w(i, j)$ are one- and two-particle operators, respectively. The Schrödinger equation for the stationary state is written as

$$H(1 \dots N) \Psi(1 \dots N) = E \Psi(1 \dots N) . \quad (3)$$

The Pauli condition for the wave function is

$$P \cdot \Psi(1 \dots N) = (-)^p \Psi(1 \dots N) , \quad (4)$$

where P is a permutation operator and $(-)^p$ is plus or minus unity depending on the parity of the operator P . The second-order density equation is written as [2]

$$\begin{aligned} E \Gamma^{(2)} &= [v(1) + v(2) + w(1, 2)] \Gamma^{(2)} \\ &+ 3 \int [v(3) + w(1, 3) + w(2, 3)] \Gamma^{(3)} dx_3 \\ &+ 6 \int w(3, 4) \Gamma^{(4)} dx_3 dx_4 , \end{aligned} \quad (5a)$$

which is equivalently written as

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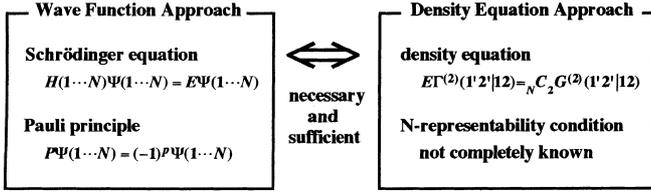


Fig. 1 Wave function method vs density equation method

$$\int [\mathcal{H}^{(2)}(12; 34) - E]\Gamma^{(4)}(1'2'3'4'|1234) dx_3 dx_4 = 0 . \quad (5b)$$

In general, the n th-order density equation is written as [2]

$$\begin{aligned} E\Gamma^{(n)} &= \left[\sum_i^n v(i) + \sum_{i>j}^n w(i, j) \right] \Gamma^{(n)} \\ &+ (n+1) \int \left[v(n+1) + \sum_i^n w(i, n+1) \right] \\ &\times \Gamma^{(n+1)} dx_{n+1} + \frac{1}{2}(n+1)(n+2) \\ &\times \int w(n+1, n+2) \Gamma^{(n+2)} dx_{n+1} dx_{n+2} , \quad (6a) \end{aligned}$$

or equivalently as

$$\begin{aligned} &\int [\mathcal{H}^{(n)}(1 \dots n; (n+1)(n+2)) - E] \\ &\times \Gamma^{(n+2)}(1' \dots (n+2)' | 1 \dots n+2) dx_{n+1} dx_{n+2} = 0 , \quad (6b) \end{aligned}$$

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

$$\begin{aligned} &\mathcal{H}^{(n)}(1 \dots n; (n+1)(n+2)) \\ &= \sum_i^n v(i) + \sum_{i>j}^n w(i, j) \\ &+ \frac{1}{2}(N-n) \left[v(n+1) + \sum_i^n w(i, n+1) \right] \\ &+ \frac{1}{2}(N-n) \left[v(n+2) + \sum_i^n w(i, n+2) \right] \\ &+ \frac{1}{2}(N-n)(N-n-1)w(n+1, n+2) , \quad (7a) \end{aligned}$$

or

$$\begin{aligned} &\mathcal{H}^{(n)}(1 \dots n; (n+1)(n+2)) \\ &= \sum_i^n v(i) + \sum_{i>j}^n w(i, j) \\ &+ (N-n) \left[v(n+1) + \sum_i^n w(i, n+1) \right] \\ &+ \frac{1}{2}(N-n)(N-n-1)w(n+1, n+2) . \quad (7b) \end{aligned}$$

$\mathcal{H}^{(n)}$ defined by Eq. (7a) is symmetric for the interchange of the coordinates, $n+1$ and $n+2$, but that by Eq. (7b) is not. The n th-order density matrix (n -DM) $\Gamma^{(n)}$ is defined by

$$\begin{aligned} &\Gamma^{(n)}(1' \dots n' | 1 \dots n) \\ &= {}_N C_n \int \Psi^*(1' \dots n'(n+1) \dots N) \\ &\times \Psi(1 \dots n(n+1) \dots N) dx_{n+1} \dots dx_N . \quad (8) \end{aligned}$$

Using the energy density matrix $G^{(n)}$, the density equation is also written as [2]

$$E\Gamma^{(n)} = {}_N C_n G^{(n)} . \quad (9)$$

The definition of $G^{(n)}$ is self-evident by comparing Eq. (9) with Eq. (6a). It was shown in the previous paper [2] that *each* density equation with $n \geq 2$ for the set of the N -representable density matrices is equivalent (connected by the *necessary and sufficient* conditions) with the Schrödinger equation constrained by the Pauli principle (see Fig. 1).

Here we note that the factor ${}_N C_n$ can be omitted if $\Gamma^{(n)}$ is normalized to unity. However, for consistence with the previous paper [2], we use the normalization given by Eq. (8).

The density equation was left unsolved, despite its potential utility, for two decades. Davidson and Harriman [5] pointed out that the number of unknowns included in the density equation is larger than the number of equations, so that the equation is insoluble. From Fig. 1, it is clear that such insolubility originates from the unknown nature of the N -representability condition: if we have the complete N -representability condition, we can solve the density equation, just as we can solve the Schrödinger equation under the Pauli condition.

Recently, a breakthrough concerning this approach was presented by Valdemoro's group [6, 7] and our group [8]. Valdemoro's group tried to find good approximate formulas representing $\Gamma^{(3)}$ and $\Gamma^{(4)}$ in terms of $\Gamma^{(2)}$ and $\Gamma^{(1)}$; putting these formulas into Eq. (5a) the density equation becomes an equation involving only $\Gamma^{(2)}$ as a basic variable. Valdemoro and her coworkers [6] generalized the fermion anticommutation relation written for the 1-DM and the first-order hole density matrix (1-HDM) to the second, third, and fourth-order cases, and from these equations they derived approximate decoupling equations (which are referred to as IPH approximation in Ref. [8]). For the 2-DM, this approximation was equivalent to the independent particle approximation. Nakatsuji and Yasuda [8], on the other hand, utilized the hierarchy equations in the Green's function method [9] and introduced the decoupling approximations which were valid essentially up to second-order in electron correlations. As clearly understood from the argument based on Fig. 1, these decoupling formulas constitute the (approximate) N -representability conditions. In this formalism, Valdemoro's approximation is shown to be valid up to first-order in the correlations. They could solve the density equation for more than ten atoms and molecules and the resultant energies and properties were in good agreement

with the full configuration interaction (CI) (exact) values. Thus, we have been able to solve the 2-DM directly from the density equation *without any use* of the wave function. Wave mechanics without wave has thus been realized in our laboratory. This was certainly a big breakthrough in the density approach in chemistry and physics.

It is therefore time to publish the time-dependent density equation. In this paper we deal with a generalization of the density equation to the time-dependent case. Our basic variable is the time-dependent density matrix which is connected with the time-dependent wave function as

$$\begin{aligned} \Gamma^{(n)} &\equiv \Gamma^{(n)}(1' \cdots n', t' | 1 \cdots n, t) \\ &= {}_N C_n \int \Psi^*(1' \cdots n'(n+1) \cdots N, t') \\ &\quad \times \Psi(1 \cdots n(n+1) \cdots N, t) dx_{n+1} \cdots dx_N \end{aligned} \quad (10)$$

and we want to derive an equation which is related to the time-dependent Schrödinger equation

$$H\Psi = i\hbar \frac{\partial}{\partial t} \Psi \quad (11)$$

by a necessary and sufficient theorem. In Sect. 2, we derive such a necessary and sufficient theorem. In Sect. 3, we give the time-dependent density equation in a form which includes only the density matrix as a variable and consider a method to use it for the direct determination of the density matrix. In Sect. 4, the perturbation theory of the density equation is studied briefly for both the time-dependent and time-independent cases. Some concluding remarks will be given in Sect. 5.

2 Basic theorem

We consider a system composed of N fermions or bosons specified by the time-dependent Hamiltonian

$$H = \sum_i^N v(i, t) + \sum_{i>j}^N w(i, j, t) , \quad (12)$$

where v and w are respectively the one- and two-particle operators which may depend explicitly on time t . We assume that our density matrix $\Gamma^{(n)}(1' \cdots n', t' | 1 \cdots n, t)$ is N -representable so that we can suppose the existence of a wave function $\Psi(1 \cdots N, t)$ which satisfies Eq. (10). Note that our time-dependent density matrix is completely general, i.e. it depends not only on the two independent sets of n -coordinates, $1' \cdots n'$ and $1 \cdots n$, but also on the two independent times, t and t' . The number of particles, N is supposed to be a constant of motion, so that

$$\int \Gamma^{(n)}(1 \cdots n, t | 1 \cdots n, t) dx_1 \cdots dx_n = {}_N C_n . \quad (13)$$

Note that

$$\int \Gamma^{(n)}(1 \cdots n, t' | 1 \cdots n, t) dx_1 \cdots dx_n = {}_N C_n S(t', t) , \quad (14)$$

where $S(t', t) = \langle \Psi(t'), \Psi(t) \rangle$.

Using the wave function Ψ introduced in Eq. (10), we define the energy density matrix for the time-dependent system analogously to Eq. (10) as,

$$\begin{aligned} G^{(n)} &\equiv G^{(n)}(1' \cdots n', t' | 1 \cdots n, t) \\ &\equiv \int [\Psi^*(1' \cdots n'(n+1)' \cdots N', t') \\ &\quad \times H(1 \cdots n(n+1) \cdots N, t) \\ &\quad \times \Psi(1 \cdots n(n+1) \cdots N, t)]_{(n+1)'=(n+1), \dots, N'=N} dx_{n+1} \cdots dx_N \\ &\equiv \langle \Psi', H\Psi \rangle_n . \end{aligned} \quad (15)$$

Note that in Eq. (15) the Hamiltonian is defined with the unprimed coordinates and time, and operates only on the right. In the last equality, the integral notation $\langle \rangle_n$ which denotes

$$\langle \rangle_n = \int [\]_{(n+1)'=(n+1), \dots, N'=N} dx_{n+1} \cdots dx_N , \quad (16)$$

is used and the prime on Ψ within $\langle \rangle_n$ means that it depends only on the primed coordinates and time, i.e. $\Psi' = \Psi(1' \cdots N', t')$. Using this notation, Eq. (10) is written as

$$\Gamma^{(n)} = {}_N C_n \langle \Psi', \Psi \rangle_n . \quad (10')$$

2.1 Theorem

The time-dependent density equation,

$$i\hbar \frac{\partial}{\partial t} \Gamma^{(n)}(1' \cdots n', t' | 1 \cdots n, t) = {}_N C_n G^{(n)}(1' \cdots n', t' | 1 \cdots n, t) \quad (17)$$

with any single n which is larger than or equal to two ($n \geq 2$) constitutes a *necessary and sufficient* condition for the $\Psi(1 \cdots N, t)$ included in Eqs. (10) and (15) to satisfy the Schrödinger equation

$$H\Psi = i\hbar \frac{\partial}{\partial t} \Psi . \quad (11')$$

2.2 Proof

We note that in Eq. (17) the operator $\frac{\partial}{\partial t}$ written by the unprimed t operates only on the unprimed time t in $\Gamma^{(n)}$. The *necessity* is as follows. From Eqs. (10) and (15), we can rewrite Eq. (17) as

$$\left\langle \Psi', \left(H - i\hbar \frac{\partial}{\partial t} \right) \Psi \right\rangle_n = 0 . \quad (18)$$

This is the density equation in the Ψ -representation. It is trivial that when Ψ satisfies Eq. (11), Eq. (18) follows automatically. Next, we prove the converse, i.e. the *sufficiency*. We first consider the lowest-order density equation with $n = 2$. Then, Eq. (17) reads

$$i\hbar \frac{\partial}{\partial t} \Gamma^{(2)}(1'2', t' | 12, t) = {}_N C_2 G^{(2)}(1'2', t' | 12, t) . \quad (19)$$

Equating $2'$ to 2 and integrating, we obtain from Eq. (19) the identity

$$i\hbar \frac{\partial}{\partial t} \Gamma^{(1)}(1', t' | 1, t) = {}_N C_1 G^{(1)}(1', t' | 1, t) , \quad (20)$$

and further

$$i\hbar \frac{\partial}{\partial t} \langle \Psi', \Psi \rangle = \langle \Psi', H\Psi \rangle . \quad (21)$$

The right-hand side of Eq. (21) can be rewritten as

$$\begin{aligned} & \langle \Psi', H\Psi \rangle \\ &= \int v(1, t) \Gamma^{(1)} dx_1 + \int w(1, 2, t) \Gamma^{(2)} dx_1 dx_2 , \quad (22) \end{aligned}$$

where we have used Eq. (12) and the permutation symmetry for the coordinates of $\Psi(1 \cdots N, t)$. We have also used the abbreviations

$$\int v(1, t) \Gamma^{(1)} dx_1 = \int [v(1, t) \Gamma^{(1)}(1', t' | 1, t)]_{1'=1} dx_1 . \quad (23)$$

Hereafter such abbreviations will be used frequently. Similarly, the integral $\langle H'\Psi', \Psi \rangle$ is written as

$$\begin{aligned} & \langle H'\Psi', \Psi \rangle \\ &= \int v^*(1', t') \Gamma^{(1)} dx_1 + \int w^*(1', 2', t') \Gamma^{(2)} dx_1 dx_2 , \quad (24) \end{aligned}$$

where v^* and w^* are actually equal to v and w , because they are real. We now introduce an N -particle function $\Phi(1 \cdots N, t)$ by

$$\Phi(1 \cdots N, t) \equiv \left[H(1 \cdots N, t) - i\hbar \frac{\partial}{\partial t} \right] \Psi(1 \cdots N, t) \quad (25)$$

and consider the integral $\langle \Phi', \Phi \rangle$:

$$\begin{aligned} \langle \Phi', \Phi \rangle &= \langle H'\Psi', H\Psi \rangle - \langle H'\Psi', i\hbar \frac{\partial}{\partial t} \Psi \rangle \\ &\quad - \langle i\hbar \frac{\partial}{\partial t} \Psi', H\Psi \rangle + \langle i\hbar \frac{\partial}{\partial t} \Psi', i\hbar \frac{\partial}{\partial t} \Psi \rangle . \quad (26) \end{aligned}$$

The first term of Eq. (26) can be transformed to

$$\begin{aligned} & \langle H'\Psi', H\Psi \rangle \\ &= {}_N C_1 \int v^*(1', t') G^{(1)}(1', t' | 1, t) dx_1 \\ &\quad + {}_N C_2 \int w^*(1', 2', t') G^{(2)}(1'2', t' | 12, t) dx_1 dx_2 \\ &= i\hbar \frac{\partial}{\partial t} \left[\int v^*(1', t') \Gamma^{(1)} dx_1 + \int w^*(1', 2', t') \Gamma^{(2)} dx_1 dx_2 \right] \\ &= i\hbar \frac{\partial}{\partial t} \langle H'\Psi', \Psi \rangle \\ &= \langle H'\Psi', i\hbar \frac{\partial}{\partial t} \Psi \rangle . \quad (27) \end{aligned}$$

The first equality was obtained similarly to Eq. (24), since Ψ and $H\Psi$ have the same symmetry for the interchange of coordinates. In the second equality we have used Eqs. (19) and (20), and in the third equality we have used Eq. (24). Next, we transform the third term of Eq. (26).

$$\begin{aligned} \left\langle i\hbar \frac{\partial}{\partial t} \Psi', H\Psi \right\rangle &= -i\hbar \frac{\partial}{\partial t} \langle \Psi', H\Psi \rangle \\ &= -i\hbar \frac{\partial}{\partial t} \left[i\hbar \frac{\partial}{\partial t} \langle \Psi', \Psi \rangle \right] \\ &= \left\langle i\hbar \frac{\partial}{\partial t} \Psi', i\hbar \frac{\partial}{\partial t} \Psi \right\rangle . \quad (28) \end{aligned}$$

In the second equality we have used Eq. (21). Inserting Eqs. (27) and (28) into Eq. (26), we obtain

$$\langle \Phi', \Phi \rangle = 0 . \quad (29)$$

for any t' and t . When $t' = t$, this is

$$\langle \Phi, \Phi \rangle = 0 \quad (30)$$

which gives $\Phi = 0$, i.e. the Schrödinger equation (Eq. 11). Thus, we have shown that the second-order density equation (Eq. 19) is a necessary and sufficient condition of the Schrödinger equation. In general, when we have the density equation (Eq. 17) with $n \geq 2$, we can always obtain the second-order density equation (Eq. 19) by a direct integration over the last $n-2$ coordinates. Therefore, the above proof also holds for the general case. Thus, we have proved that the time-dependent density equation (Eq. 17) with any single $n(n \geq 2)$ is a necessary and sufficient condition for the Ψ to satisfy the time-dependent Schrödinger equation (Eq. 11). (QED)

2.3 Implication of the theorem

Because the theorem is a necessary and sufficient theorem, it shows that the density equation (Eq. 17) for any single $n(n \geq 2)$ is just *equivalent* to the Schrödinger equation (Eq. 11) so long as the density matrix is N -representable. Among others, the simplest equation is the second-order density equation (Eq. 19) with $n = 2$. Here, the density equation is defined using Ψ explicitly, but our purpose is to solve the density equation not in the Ψ -space but for the set of the density matrices. For this purpose, we have to transform the energy density matrix $G^{(n)}$ such that it depends only on the density matrix, since $G^{(n)}$ was defined in Eq. (15) using the wave function Ψ . Such a transformation will give an equation-of-motion of the N -representable density matrix itself, as will be shown in the next section.

The following properties of the density equation are important:

1. As in the time-independent case, the equation for $n = 1$ (first-order equation) is not a sufficient condition, though it is evidently a necessary condition. This is due to the fact that our Hamiltonian (Eq. 12) includes up to the two-particle interaction terms. For the case in which the Hamiltonian is composed of only the one-particle term (e.g. the model Hamiltonian in the time-dependent Hartree-Fock theory), the first-order density equation also constitutes a necessary and sufficient condition.
2. In general, when the Hamiltonian of the system includes up to p -particle interaction operators, it is

easy to show that the necessary and sufficient theorem holds for the density equation higher than the p -th order ($n \geq p$).

3. The permutation symmetry of the wave function Ψ required in the proof of the theorem was only for the three types of exchange operators, P_{12} , P_{1i} and P_{2i} ($3 \leq i \leq N$), in the pairwise exchanges in both sides of bra and ket, i.e.

$$(P\Psi)^*P\Psi = \Psi^*\Psi, \quad P = P_{12}, \quad P_{1i}, \quad P_{2i} \quad (3 \leq i \leq N). \quad (31)$$

Although this requirement alone looks at first sight to be much weaker than requiring Ψ to be symmetric or antisymmetric for any exchange operators (i.e. requiring Γ to be N -representable), it can be shown that these two requirements are the same¹ [10]. Therefore, the theorem is valid only for the N -representable set of the density matrices.

4. When the system is time-independent, the present time-dependent density equation reduces to the previous time-independent density equation. For the stationary state, the time variable would appear as

$$\Psi(1 \cdots N, t) = \Phi(1 \cdots N) e^{-iEt/\hbar}, \quad (32)$$

or

$$\Gamma^{(n)}(1' \cdots n', t' | 1 \cdots n, t) = \Gamma^{(n)}(1' \cdots n' | 1 \cdots n) e^{-iE(t-t')/\hbar} \quad (33)$$

$$G^{(n)}(1' \cdots n', t' | 1 \cdots n, t) = G^{(n)}(1' \cdots n' | 1 \cdots n) e^{-iE(t-t')/\hbar} \quad (34)$$

where E is an appropriate constant. Inserting these equations into Eq. (17), we obtain

$$E\Gamma^{(n)}(1' \cdots n' | 1 \cdots n) = {}_N C_n G^{(n)}(1' \cdots n' | 1 \cdots n) \quad (9)$$

which is just the density equation for the time-independent system, and the constant E is the energy of the system given by

$$E = \int G^{(n)}(1 \cdots n | 1 \cdots n) dx_1 \cdots dx_n. \quad (35)$$

3 Time-dependent density equation

In this section, we transform the time-dependent density equation (Eq. 17) into the form which includes only the density matrix as a self-contained variable, and consider

¹ The requirement given by Eq. (31) means that the Ψ should be symmetric or antisymmetric for the exchanges P_{12} , P_{1i} and P_{2i} ($3 \leq i \leq N$). However, this requirement is completely general: any exchange operator P_{jk} can be written as $P_{jk} = P_{1j} P_{2k} P_{12} P_{2k} P_{1j}$, so that such Ψ should actually be an eigenfunction of *any* exchange operators, all of the eigenvalues being either $+1$ or -1 . (See, e.g. Ref. [10]. Since any permutation operator can be written as a product of exchange operators, the requirement given by Eq. (31) is completely general. (In a previous paper (Ref. 2), the author has tried to expand the space of the density matrix from the N -representable one in the last two paragraphs of Sect. IIIA, but the resultant space turned out to be *not* wider than the N -representable space for the reason given above.)

the method to use the density equation for the direct determination of the density matrix.

We rewrite the Hamiltonian of the system given by Eq. (12) as

$$H = \sum_{i=1}^n v(i, t) + \sum_{i>j}^n w(i, j, t) + \sum_{i=n+1}^N \left[v(i, t) + \sum_{j=1}^n w(i, j, t) \right] + \sum_{i>j \geq n+1}^n w(i, j, t). \quad (36)$$

Inserting Eq. (36) into the density equation (Eq. 17) or (Eq. 18) and performing the integration over the last $N - n$ coordinates, we obtain the density equation in the form

$$\int \left[\mathcal{H}^{(n)}(1 \cdots n; (n+1)(n+2) : t) - i\hbar \frac{\partial}{\partial t} \right] \Gamma^{(n+2)} dx_{n+1} dx_{n+2} = 0, \quad (37)$$

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

$$\begin{aligned} \mathcal{H}^{(n)}(1 \cdots n; (n+1)(n+2) : t) &= \sum_i^n v(i, t) + \sum_{i>j}^n w(i, j, t) \\ &+ \frac{1}{2}(N-n) \left[v(n+1, t) + \sum_i^n w(i, n+1, t) \right] \\ &+ \frac{1}{2}(N-n) \left[v(n+2, t) + \sum_i^n w(i, n+2, t) \right] \\ &+ \frac{1}{2}(N-n)(N-n-1)w(n+1, n+2, t), \end{aligned} \quad (38a)$$

or

$$\begin{aligned} \mathcal{H}^{(n)}(1 \cdots n; (n+1)(n+2) : t) &= \sum_i^n v(i, t) + \sum_{i>j}^n w(i, j, t) \\ &+ (N-n) \left[v(n+1, t) + \sum_i^n w(i, n+1, t) \right] \\ &+ \frac{1}{2}(N-n)(N-n-1)w(n+1, n+2, t). \end{aligned} \quad (38b)$$

In Eq. (37), we have used the abbreviation as in Eq. (23). As the reduced Hamiltonian, we may use either Eq. (38a) or (38b). The former is symmetric for the coordinates $n+1$ and $n+2$, but the latter is not. The two particles $n+1$ and $n+2$ are the representatives of the last $N - n$ particles.

The density equation (Eq. 37) is written in a following equivalent form. Using the recurrence formula for the density matrix

$$\begin{aligned} \int \Gamma^{(p)}(1' \cdots (p-1)' p, t' | 1 \cdots (p-1) p, t) dx_p \\ = \frac{N-p+1}{p} \Gamma^{(p-1)}(1' \cdots (p-1)', t' | 1 \cdots (p-1), t), \end{aligned} \quad (39)$$

we can rewrite Eq. (37) as

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \Gamma^{(n)} &= \left[\sum_i^n v(i, t) + \sum_{i>j}^n w(i, j, t) \right] \Gamma^{(n)} \\
&+ (n+1) \int \left[v(n+1, t) + \sum_i^n w(i, n+1, t) \right] \\
&\times \Gamma^{(n+1)} dx_{n+1} + \frac{1}{2} (n+1)(n+2) \\
&\times \int w(n+1, n+2, t) \Gamma^{(n+2)} dx_{n+1} dx_{n+2} . \quad (40)
\end{aligned}$$

From the previous theorem, the density equation (Eq. 17), (Eq. 37) or (Eq. 40) with any single n ($n \geq 2$) is equivalent to the Schrödinger equation for the set of the N -representable density matrices. That is, to solve the Schrödinger equation (Eq. 11) imposing Ψ to be symmetric (for bosons) or antisymmetric (for fermions) is equivalent to solving the density equation (Eq. 17), (Eq. 37) or (Eq. 40) imposing the density matrix to be N -representable. This equivalence is just like the one shown in Fig. 1 for the time-independent case. The density equation gives the exact density matrix without any ambiguity when it is solved for the N -representable ones. Thus, the time-dependent density equation (Eq. 37) or (Eq. 40) is self-contained equation for the time-dependent density matrix, and so may be considered as giving an equation-of-motion of the N -representable density matrix. There, *every* solution of the density equation should be identical with the one obtained indirectly from the Schrödinger equation.

The simplest and practically most important density equation is the second-order density equation given by

$$\begin{aligned}
&\int \left[\mathcal{H}^{(2)}(12; 34 : t) - i\hbar \frac{\partial}{\partial t} \right] \\
&\times \Gamma^{(4)}(1'2'3'4' : t | 1234, t) dx_3 dx_4 = 0 , \quad (41)
\end{aligned}$$

or

$$\begin{aligned}
i\hbar \frac{\partial}{\partial t} \Gamma^{(2)} &= [v(1, t) + v(2, t) + w(1, 2, t)] \Gamma^{(2)} \\
&+ 3 \int [v(3, t) + w(1, 3, t) + w(2, 3, t)] \Gamma^{(3)} dx_3 \\
&+ 6 \int w(3, 4, t) \Gamma^{(4)} dx_3 dx_4 . \quad (42)
\end{aligned}$$

Here, the variable is essentially the 2-DM $\Gamma^{(2)}$ irrespective of the number of the particles involved in the system. This would be a quite remarkable simplification over the Schrödinger equation in which the variable Ψ depends on all the N coordinates. In the density equation, N is included in the reduced Hamiltonian only as a constant factor, so that an increase in N would not cause a difficulty in solution. In the Schrödinger equation, however, it is well known that an increase in N causes a tremendous difficulty in solution.

A note is necessary here that the density equation (Eq. 41) or (Eq. 42) involve not only $\Gamma^{(2)}$ but also $\Gamma^{(3)}$ and $\Gamma^{(4)}$ so they are indeterministic by themselves. However, the necessary and sufficient relation as given in the proof and as depicted in Fig. 2 means that they are deterministic when the complete N -representability condition is given as a subsidiary condition. This implies that the N -representability condition describes the explicit and exact relations of $\Gamma^{(3)}$ and $\Gamma^{(4)}$ in terms of $\Gamma^{(2)}$ and $\Gamma^{(1)}$.

The density equation given by Eq. (40) or (42) is similar to a member of the coupled chain of hierarchy equations often appearing in the many-body theory (e.g. Green's function) [9, 11]. We also refer to the BBKGY (Born-Bogoliubov-Kirkwood-(H. S.) Green-Yvon) equation (see, for example, Ref. [12]). In particular, in the time-independent limit, Eq. (40) becomes identical with a member of the coupled hierarchy equations derived for the density matrix by Cho [13] and by Cohen and Frishberg [14], who showed only the necessary condition. However, the implication of our density equation is essentially different from that of these hierarchy equations. As discussed in the previous paragraph, *every* density equation higher than second order is *deterministic* in that it is equivalent to (a necessary and sufficient condition of) the Schrödinger equation. The higher-order equations are not required for the exact solution in contrast to the usual interpretation of the hierarchy equations.

So far, we have supposed that our density equation is to be solved for the N -representable density matrix. In such a case, all the solutions would be the exact physical solutions. However, since the complete (necessary and sufficient) N -representability conditions are not yet known at present, such a presupposition would not be realistic. So, we may relax the constraint, i.e. we solve the density equation imposing only the known and tractable N -representability conditions. Such a procedure is possible for the density equation since it is a non-variational equation. Even in such a case, the density equation would give correct exact solutions within the N -representable set, though it may also give some non-physical solutions in the space *outside* of the N -representable set. The properties and the number of these non-physical solutions would depend strongly on the N -representability (necessary) conditions which have been imposed simultaneously on the density equation. These non-physical solutions could be eliminated, in principle, using the rest of the N -representability conditions, although we are not sure whether the already known N -representability conditions are enough for completely eliminating these non-physical solutions. In some cases, the experimental values for some properties of the system may well be used, since our knowledge on the complete N -representability condition is still limited.

In the above procedure, the choice of the N -representability conditions to be imposed simultaneously on the density equation are very important, in order to *effectively* reduce the non-physical solutions. If the choice is improper, the number of the non-physical solutions would be too many to select out the correct ones. Nevertheless, the above procedure would be more realistic than the variational solution for which the *complete* N -

representability conditions are required *before* solution in order to obtain a correct upper bound of the energy². In the density equation, some of the conditions may be used *after* solution for selecting the correct solutions. Such a procedure seems furthermore to be more convenient since some of the known N -representability conditions are too complex to be used as simultaneous constraints. They are more easily used as the criteria of the N -representability for the *given* density matrix obtained as a solution.

In the previous solution of the time-independent density equation [8], the 3- and 4-DM, $\Gamma^{(3)}$ and $\Gamma^{(4)}$, were decoupled with the use of $\Gamma^{(2)}$ and $\Gamma^{(1)}$, using the Green's function technique for the correlation expansion correct up to the second-order. Though our formulas might be far from the correct N -representability condition, they certainly worked for many molecules in calculating the 2-DM without any use of wave functions. The calculated $\Gamma^{(1)}$ and $\Gamma^{(2)}$ were completely N -representable and almost N -representable, respectively. A similar method of solution is expected for the time-dependent density equation.

4 Perturbation theory for the density equation

We next consider the perturbation theory for both the time-dependent and time-independent density equations. We refer to the earlier perturbation theory formulation for the density matrix [16, 17]. When the Hamiltonian of the system is divided into the unperturbed part and the perturbation part

$$H = H_0 + \lambda H_1 \quad (43)$$

the reduced Hamiltonian given by Eq. (38) is divided similarly as

$$\mathcal{H}^{(n)} = \mathcal{H}_0^{(n)} + \lambda \mathcal{H}_1^{(n)} \quad (44)$$

where $\mathcal{H}_0^{(n)}$ and $\mathcal{H}_1^{(n)}$ have the same form as Eq. (38) except that they are composed of v_0 , w_0 and v_1 , w_1 , respectively. When the perturbation is the so-called one-particle perturbation, $\mathcal{H}_1^{(n)}$ is composed only of the operator v_1 , and the application would be simplified. As in the conventional perturbation theory in the Ψ -space, we assume that the density matrix $\Gamma^{(n+2)}$ is expanded in power series in the perturbation parameter λ

$$\Gamma^{(n+2)} = \sum_{k=0} \lambda^k \Gamma_k^{(n+2)} \quad (45)$$

where k denotes the order of the perturbation.

4.1 Time-dependent case

Inserting Eqs. (44) and (45) into the density equation (Eq. 37), and equating the coefficient of each power in λ to be zero, we obtain

² Garrod and Percus have proposed a variational method in which only the selected N -representability conditions are used to get the lower bound to the ground state energy. (see Ref [15]).

$$\int \left(\mathcal{H}_0^{(n)} - i\hbar \frac{\partial}{\partial t} \right) \Gamma_0^{(n+2)} dx_{n+1} dx_{n+2} = 0, \quad (46)$$

which is the density equation for the unperturbed system, and

$$\int \left[\left(\mathcal{H}_0^{(n)} - i\hbar \frac{\partial}{\partial t} \right) \Gamma_k^{(n+2)} + \mathcal{H}_1^{(n)} \Gamma_{k-1}^{(n+2)} \right] dx_{n+1} dx_{n+2} = 0, \quad (k = 1, 2, \dots) \quad (47)$$

which is the density equation for the k th-order correction, $\Gamma_k^{(n+2)}$. The normalization condition for the density matrix (Eq. 13) gives

$$\int \Gamma_0^{(n+2)} (1 \cdots n+2, t | 1 \cdots n+2, t) dx_1 \cdots dx_{n+2} = {}_N C_{n+2}, \quad (48)$$

and

$$\int \Gamma_k^{(n+2)} (1 \cdots n+2, t | 1 \cdots n+2, t) dx_1 \cdots dx_{n+2} = 0, \quad (k = 1, 2, \dots) \quad (49)$$

When the unperturbed Hamiltonian $\mathcal{H}_0^{(n)}$ is time independent, the solution of Eq. (46) may be written in the form given by Eq. (33).

4.2 Time-independent case

Here, we further assume, in addition to Eq. (45), that the energy E of the perturbed system is expanded as

$$E = \sum_{k=0} \lambda^k E_k. \quad (50)$$

Inserting Eqs. (45) and (50) into the time-independent density equation (Eq. 6b), we obtain a set of equations

$$\int (\mathcal{H}_0^{(n)} - E_0) \Gamma_0^{(n+2)} dx_{n+1} dx_{n+2} = 0, \quad (51)$$

$$\int [(\mathcal{H}_0^{(n)} - E_0) \Gamma_1^{(n+2)} + (\mathcal{H}_1^{(n)} - E_1) \Gamma_0^{(n+2)}] \times dx_{n+1} dx_{n+2} = 0, \quad (52)$$

and

$$\int \left[(\mathcal{H}_0^{(n)} - E_0) \Gamma_k^{(n+2)} + (\mathcal{H}_1^{(n)} - E_1) \Gamma_{k-1}^{(n+2)} - \sum_{j=2}^k E_j \Gamma_{k-j}^{(n+2)} \right] \times dx_{n+1} dx_{n+2} = 0, \quad (k = 2, 3, \dots) \quad (53)$$

where Eq. (51) is the equation for the unperturbed system, Eq. (52) the equation for the first-order correction to the density matrix, and Eq. (53) the equation for the k th-order correction. The normalization condition gives the same equations as Eqs. (48) and (49).

The expression of the k th-order correction to the energy, E_k is obtained by integrating Eqs. (52) and (53). It includes both of the k th- and $(k-1)$ th-order corrections, $\Gamma_k^{(n+2)}$ and $\Gamma_{k-1}^{(n+2)}$. However, we show below that we need only $\Gamma_{k-1}^{(n+2)}$ for the calculation of E_k . The energy of the perturbed system is written as

$$E = ({}_N C_{n+2})^{-1} \int \mathcal{H}^{(n)} \Gamma^{(n+2)} dx_1 \cdots dx_{n+2} . \quad (54)$$

We use the Hellmann-Feynman theorem in the form

$$\frac{\partial E}{\partial \lambda} = ({}_N C_{n+2})^{-1} \int \frac{\partial \mathcal{H}^{(n)}}{\partial \lambda} \Gamma^{(n+2)} dx_1 \cdots dx_{n+2} , \quad (55a)$$

or

$$\int \mathcal{H}^{(n)} \frac{\partial \Gamma^{(n+2)}}{\partial \lambda} dx_1 \cdots dx_{n+2} = 0 , \quad (55b)$$

where λ is a dummy perturbation parameter defined in Eq. (43). Differentiating Eq. (50) with respect to λ , equating the result with Eq. (55a), and making the coefficient of each power of λ zero, we obtain

$$E_k = ({}_k C_{n+2})^{-1} \int \mathcal{H}_1^{(n)} \Gamma_{k-1}^{(n+2)} dx_1 \cdots dx_{n+2} . \quad (56)$$

$(k = 1, 2, \dots)$

This equation requires only $\Gamma_{k-1}^{(n+2)}$ for the calculation of E_k which somewhat reduces the labour in calculating the perturbation energy. Further, the Hellmann-Feynman theorem expressed by Eq. (55b) gives the equations

$$\int \mathcal{H}_0^{(n)} \Gamma_1^{(n+2)} dx_1 \cdots dx_{n+2} = 0 , \quad (57a)$$

and

$$k \int \mathcal{H}_0^{(n)} \Gamma_k^{(n+2)} dx_1 \cdots dx_{n+2} + (k-1) \int \mathcal{H}_1^{(n)} \Gamma_{k-1}^{(n+2)} dx_1 \cdots dx_{n+2} = 0 , \quad (57b)$$

which shows an interrelation between the k th- and $(k-1)$ th-order corrections. The expression corresponding to Eq. (56) was derived in the Ψ -representation by Carr [18] and Löwdin [19].

5 Concluding remarks

In this paper, the author has generalized the density equation to the time-dependent case and obtained an equation-of-motion for the N -representable density matrix. The equation has the form which is formally obtainable from the previous time-independent equation by replacing E with $i\hbar \partial/\partial t$. Its properties are also similar to the previous ones. Therefore, some of the previous results are easily extended to the time-dependent case. An example is the time-dependent Hartree-Fock equation [20] which is easily derived from the present time-dependent density equation by using the independent particle approximation, just like the Hartree-Fock equation derived from the density equation in a previous paper [2]. The equation for the correlated

density [2] is also easily extended to the time-dependent case.

The perturbation theory for the density equation would be useful when the density equation for the unperturbed system is solved exactly. When we take electron correlation as a perturbation, the Hartree-Fock equation which is the unperturbed density equation [2], and the correlated density equation [2], which includes the correlation correction to all orders, may be divided into each order using the present perturbation theory.

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