Direct determination of the quantum-mechanical density matrix using the density equation. II.

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With the use of the density equation [Phys. Rev. A **14**, 41 (1976)], second-order density matrices of atoms and molecules are calculated directly without any use of the wave function. The decoupling of the third- and fourth-order density matrices is done using the diagrammatic procedure of the Green's-function method, including terms up to second order in electron correlation. In addition to the results given in a previous communication [Phys. Rev. Lett. **76**, 1039 (1996)], we give more detailed formulations, discussions, and additional results for H_2O, NH_3, CH_4, HF, N_2, CO, and acetylene using double-ζ basis sets, and for CH_3OH, CH_3NH_2, and C_2H_6 (staggered and eclipsed) using minimal basis sets. The present density-equation method gave energies as accurate as, and reduced density matrices (RDM's) more accurate than the single and double excitation configuration interaction method. The present method seems to give better quality results as the system becomes large. The convergence was fairly good and the calculated second-order RDM's almost satisfied some necessary conditions of the N representability, the so-called P, Q, and G conditions, while the first-order RDM's were exactly N representable. The variety of the molecules calculated and the quality of the calculated results show that the density-equation method can be a promising alternative to the wave-function approach in quantum mechanics. [S1050-2947(97)06409-3]

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I. INTRODUCTION

Since all the operators we shall concern ourselves with in quantum mechanics are one- and two-body ones, all the elemental physical quantities can be calculated from the second-order density matrix (2-DM). Many-electron wave functions involve more information than we need to know. Thus a determination of the density or density matrices without using the wave function could be a convenient alternative to the wave mechanics, and this approach is often called "wave mechanics without wave." Since the 2-DM determines the energy, we may apply the variational principle in a suitable domain of the density matrices [1]. However, it is still not completely known what conditions the Pauli principle enforces on the density matrices (the N-representability condition) [2]. Moreover, since these conditions may be very complicated, it would be impractical to carry out such variational calculations.

One of the authors proposed a nonvariational approach for a direct determination of the density matrix [3]. He showed that the equation

$$E\Gamma^{(n)} = \left\{ \sum_i^n v(i) + \sum_{i>j}^n w(i,j) \right\} \Gamma^{(n)} + (n+1) \int \left\{ v(n+1) + \sum_i^n w(i,n+1) \right\} \Gamma^{(n+1)} dx_{n+1}$$

$$+ \tfrac{1}{2}(n+1)(n+2) \int w(n+1,n+2) \Gamma^{(n+2)} dx_{n+1} dx_{n+2}, \tag{1.1}$$

which is called the density equation, is *equivalent* to the Schrödinger equation in the domain of N-representable DM's *for each n with $n \geq 2$*. That is, this equation in the domain of the N-representable space is a *necessary and sufficient* condition for the corresponding antisymmetric wave function to satisfy the Schrödinger equation. The necessity alone was shown by Cho and by Cohen and Frishberg [4]. Unfortunately, since the nth-order density equation contains nth, $(n+1)$th, and $(n+2)$th order DM's, that is, the number of the unknowns exceeds the number of the conditions as far as the N representability condition is not completely known, the solution of the density equation itself is not unique [5]. However, the solution within the N-representable space is guaranteed to be exact, and we use the subsidiary N-representability conditions to eliminate unphysical solutions.

On the other hand, if we can approximate $(n+1)$th- and $(n+2)$th-order DM's using the nth- and lower-order ones, we can directly determine the density matrix from the den-

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sity equation without using the wave function. Actually, the equivalence of the Schrödinger equation plus Pauli principle with the density equation plus N representability condition [3] implies that the N representability condition has a power of expressing $\Gamma^{(n+2)}$ and $\Gamma^{(n+1)}$ in terms of $\Gamma^{(n)}$. Thus, the above approximation also works as the N-representability condition. In principle, the ground-state nth-order DM determines the DM's of all orders including the wave function, since it determines the electron density and hence the wave function (Hohenberg-Kohn theorem [6]).

Recently, Valdemoro and co-workers [7,8] reported an interesting approach for solving the density equation. They suggested a decoupling approximation of higher-order reduced density matrices (RDM's) in terms of the lower-order ones based essentially on the fermion's anticommutation relations. They derived the identity containing the n-RDM and n-hole RDM (HRDM) on the left-hand side (LHS), and the lower-order RDM's and HRDM's on the right-hand side (RHS), and then assumed that the n-RDM (n-HRDM) on the lhs is equal to the sum of the products of the lower-order RDM's (HRDM's) on the rhs. We call this approximation the IPH approximation (the approximation identifying the particle and hole parts separately). With this approximation, Colmenero and Valdemoro solved the density equation [9] for some four- and six-electron systems, and calculated their density matrices directly [10]. However, their results seem to have been limited to small systems, and the applicability to general many-electron systems is an open question. Since their decoupling approximation is accurate for a Be atom (four-electron system) but less accurate for H_2O (ten-electron system) [8], we have to look for a more accurate approximation which is suitable for studying more complex atoms and molecules.

In a previous paper [11], we proposed a different approach for solving the density equation: we presented the decoupling approximation based on the Green's-function technique, and applied it using the second-order density equation [Eq. (1.1) with $n=2$] to directly determine the 2-RDM's of several atoms and molecules. We found that our method is very promising, giving as accurate energies as, and more accurate density matrices than, those of the variational SDCI (single and double excitation configuration interaction) one. We checked some N-representability conditions, and found that the resultant 2-RDM's almost satisfied these conditions, while the 1-RDM's were exactly N representable. This success opened a possibility of an entirely new method in quantum mechanics, and gave us some insight into the N-representability conditions.

In this paper we give more detailed explanations of the approximations for expressing the 3- and 4-RDM's in terms of the 1- and 2-RDM's, which were discussed briefly in the previous paper [11], show some new results, and discuss the convergence properties of our method.

II. APPROXIMATIONS OF 3- AND 4-RDM'S

We use the Green's-function (GF) method to derive approximate relations of the higher-order DM's with the lower-order ones. The IPH approximation is derived as a special case. The DM's are defined as [12]

$$\Gamma^{(n)}(x_1' \cdots x_n' | x_1 \cdots x_n)$$
$$= \frac{1}{n!} \langle \phi^\dagger(x_1) \cdots \phi^\dagger(x_n) \phi(x_n') \cdots \phi(x_1') \rangle. \tag{2.1}$$

where x_i denotes space-spin coordinate of i-th electron, while $\phi^\dagger$ and ϕ denote creation and annihilation field operators, respectively. The n-RDM's are defined as

$$^nD(r_1' \cdots r_n' | r_1 \cdots r_n)$$

$$= \sum_{\sigma_1 \cdots \sigma_n} \Gamma^{(n)}(x_1' \ldots x_n' | x_1 \ldots x_n) \tag{2.2}$$

where r_i and σ_i denote space and spin coordinates, respectively. The n-particle many-body GF's are defined as [13]

$$G^{(n)}(x_1' t_1' \cdots x_n' t_n' | x_1 t_1 \cdots x_n t_n)$$

$$= (-i)^n \langle T[\phi(x_1' t_1') \cdots \phi(x_n' t_n') \phi^\dagger(x_n t_n) \cdots \phi^\dagger(x_1 t_1)] \rangle \tag{2.3}$$

where T denotes the time ordering operator. The DM's are related to the GF's as

$$\Gamma^{(n)}(x_1' \cdots x_n' | x_1 \cdots x_n)$$
$$= \frac{(-i)^n}{n!} G^{(n)}(x_1' 0^- \cdots x_n' 0^- | x_1 0^+ \cdots x_n 0^+), \tag{2.4}$$

where 0^+ and 0^- denote positive and negative infinitesimals, respectively. They determine the time ordering of the operators in Eq. (2.3) so as to match the definition of the DM's given by Eq. (2.1).

Later we use matrix notations of these quantities, where the subscript j_k and the superscript i_k are associated with the annihilation and creation operators, respectively, and the one-particle basis function is a spin-orbital for the DM and a spatial orbital for the RDM.

In order to obtain the relations among the GF's, we first consider the lower-order perturbation series, and then include some higher-order effects. We use Feynman's procedure, which represents the GF as a sum of the topologically different diagrams [13]. After taking the limit of time variables to get the relations among the DM's, we rewrite them into the relations among the RDM's by summing up the spin variables. We use the Hartree-Fock (HF) GF's as unperturbed zeroth-order GF's, and the electron correlation is treated as a perturbation. Hence our approximation works best for closed-shell atoms and molecules, dealing mainly with the dynamic correlations.

A. Approximation of the 4-RDM

There are four kinds of diagrams for the four-particle GF up to the second order in the perturbation. In a standard diagrammatic notation, they are represented symbolically as

$$G^{(4)}$$

$$(2.5)$$

in which the coefficient for the kth-order perturbation diagram of $G^{(n)}$ is $\pm i^{m-k-n}$, where m is the number of the HF GF's in the diagram, and the relative sign ensures the permutational antisymmetry [13]. With the use of the lower-order relations which connect $G^{(3)}$ with $G^{(2)}$ and $G^{(1)}$, and $G^{(2)}$ with $G^{(1)}$, it is easy to show that the sum of the first, second, and third terms of Eq. (2.5) reproduces the IPH approximation for the 4-RDM [8]: the last term missing in the IPH approximation represents the simultaneous collisions of two electron pairs, so that we call it two-pair (2P) term. It is a central term in the independent pair model which is a good approximation for describing the dynamic correlations in atoms and molecules [14]. The third term in Eq. (2.5) will be considered in the approximation of the 3-RDM.

The 2P term is calculated as follows: for a given 2-DM, the collision term U is defined as

$$U(x_1'x_2'|x_1x_2) - U(x_1'x_2'|x_2x_1)$$
$$= 2\Gamma^{(2)}(x_1'x_2'|x_1x_2) - \begin{vmatrix} \Gamma^{(1)}(x_1'|x_1) & \Gamma^{(1)}(x_1'|x_2) \\ \Gamma^{(1)}(x_2'|x_1) & \Gamma^{(1)}(x_2'|x_2) \end{vmatrix}.$$

$$(2.6)$$

Except for a coefficient, it is represented as

$$U(x_1'x_2'|x_1x_2) = $$

$$(2.7)$$

in which the bold line is the exact one-particle GF, while the rectangle is the exact vertex of $G^{(2)}$ [13]. In the above figure we replaced the time variables in the external lines with positive and negative infinitesimals. The term U represents the sum of the collisions of two electrons which cannot be written by simple products of the 1-DM's. Similarly, the 2P term represents independent collisions of two electron pairs, and is written as the sum of the permuted, antisymmetrized products of U:

$$^{2P}\Gamma^{(4)} = \frac{1}{4!} U_{j1,j2}^{i1,i2} U_{j3,j4}^{i3,i4} + \cdots . \qquad (2.8)$$

To generate all the terms in Eq. (2.8), we substitute four indices (i_1, i_2, i_3, and i_4) of three terms $U_{j1,j2}^{i1,i2}U_{j3,j4}^{i3,i4}$, $U_{j1,j3}^{i1,i3}U_{j2,j4}^{i2,i4}$, and $U_{j1,j4}^{i1,i4}U_{j2,j3}^{i2,i3}$ in all possible ways (4!). Then we obtain the topologically different diagrams for the 2P term whose total number is 72.

Since our Hamiltonian is spin independent, and since our present subjects are closed-shell atoms and molecules, $G^{(1)}$

becomes a unit operator $\delta_\sigma^{\sigma'}$ in a spin space. The spin sum yields a factor of 2^{4-p} for each permuted diagram of 4-RDM, where p is a parity of the permutational group. For example, the spin sum of $U_{j1,j3}^{i1,i4}U_{j2,j4}^{i3,i2}$ yields a factor of 2^2.

In the present approximation, the 4-RDM includes all four kinds of diagrams in Eq. (2.5) and some higher-order terms, because U is calculated from the 2-DM itself. In the direct determination of the 2-RDM described in Sec. III, this approximate 4-RDM is used to calculate the rhs of the density equation (1.1), then this equation is used to calculate a new 2-RDM. Through this self-consistency process, the 2-RDM, U, and the approximate 4-RDM come to include some higher-order terms.

The lowest-order missing terms in the present approximation of the 4-RDM are represented symbolically as

$$(2.9)$$

which are third-order and are not represented by the simple products of the lower-order RDM's.

B. Approximation for the 3-RDM

There are three kinds of diagrams of the three-particle GF up to second order in the perturbation, and they are represented symbolically as

$$G^{(3)} = $$ $$(2.10)$$

With the use of the lower-order relations, we can show that the sum of the first and second terms of Eq. (2.10) reproduces the IPH approximation for the 3-RDM. The last term of Eq. (2.10) is second order in the perturbation of the electron correlation, and may not be negligible. To approximate it, including not only the lowest-order term but also some higher-order terms, we use Dyson's equation and the property of the unperturbed GF's.

An exact one-particle GF satisfies the Dyson's integral equation

 $$(2.11)$$

where an open circle means the irreducible self-energy which is an energy-dependent effective one-body potential due to the electron interaction [13]. The second term then represents the multiple scattering by the self-energy.

The HF GF which we use as the zeroth order unperturbed one is written as [13]

$$G_0^{(1)}(x't',xt)$$

$$= +i \sum_k^{\text{occupied}} \varphi_k^*(x)\varphi_k(x')\exp[-i\epsilon_k(t'-t)]; \qquad t' \lessgtr t$$

$$- i \sum_k^{\text{unoccupied}} \varphi_k^*(x)\varphi_k(x')\exp[-i\epsilon_k(t'-t)]; \quad t' \gtrless t,$$

$$\tag{2.12}$$

where φ_k and ϵ_k are the HF orbital and orbital energy, respectively. Since this unperturbed GF describes the probability amplitude of each independent electron (hole) from xt to $x't'$ (and vice versa), it satisfies the rule of the probability amplitude on the subsequent events in the path-integral theory [15]. Hence it has the property

$$\int dy\, G_0^{(1)}(zt',y0)G_0^{(1)}(y0,xt)$$

$$= (-i)G_0^{(1)}(zt',xt); \quad t' \geq 0 \geq t$$

$$(+i)G_0^{(1)}(zt',xt); \quad t' \leq 0 \leq t,$$

$$\tag{2.13}$$

in which we integrate all the intermediate states, $y0$. The space integration of the two GF's gives one GF in these time orderings. From the definition of the HF GF, Eq. (2.12), only the occupied (unoccupied) orbitals contribute to $G_0^{(1)}$ when $t' < t$ $(t' > t)$. Since these two kinds of orbitals are orthonormal to each other, the relative sign in Eq. (2.13) can be treated with the use of the projector,

$$P(y) = i\left(\sum_k^{\text{unoccupied}} - \sum_k^{\text{occupied}} \right)|\varphi_k(y)\rangle\langle\varphi_k(y)|. \tag{2.14}$$

Then Eq. (2.13) becomes

$$\int dy\, G_0^{(1)}(zt',y0)P(y)G_0^{(1)}(y0,xt)$$

$$= G_0^{(1)}(zt',xt); \qquad tt' < 0, \tag{2.15}$$

which we represent in a diagrammatic form as

$$\triangle \quad = \quad | \quad ; \quad tt' < 0, \tag{2.16}$$

where the triangle means the projector P. We note that Eqs. (2.15) and (2.16) are valid only when $tt' < 0$: the lhs's of Eqs. (2.15) and (2.16) vanish identically when $tt' > 0$, while their rhs's do not. Note that only space integration for y is necessary, in contrast to the ordinary space-time integration in the GF theory.

It is well known that the exact GF has an expression similar to Eq. (2.12) (the Lehmann representation). One-particle functions which contribute to $G^{(1)}$ when $t' > t$ $(t' < t)$ correspond to the quasiparticle wave functions of anion (ionized) states. However, since these functions are not orthonormal, the exact $G^{(1)}$ does not have an expression like Eq. (2.15).

With the use of Dyson's equation (2.11) and the HF GF's property (2.16), the last term of Eq. (2.10) is transformed as

$$\tag{2.17}$$

where the approximation means that it is valid only when $tt' < 0$. The case $tt' > 0$ will be considered later. The term expressed by Eq. (2.17) is called the UV term. The only unknown in the above figure which we call the V term is similarly approximated as

$$\tag{2.18}$$

After manipulating some numerical coefficients, the UV term given by diagram (2.17) is written into an ordinary formula as

$$^{UV}\Gamma^{(3)i1,i2,i3}_{j1,j2,j3} = \tfrac{1}{6}(V^{i1,i2}_{j1,l2}P^{l2}_{k2}U^{k2,i3}_{j2,j3} + \cdots)$$

$$= \tfrac{1}{6}(VPU + \cdots). \tag{2.19}$$

From diagram (2.18), the V term is written as

$$V^{i1,i2}_{j1,j2} = U^{i1,i2}_{j1,j2} + V^{i1,i2}_{j1,l2}P^{l2}_{k2}(\Gamma^{(1)k2}_{j2} - \Gamma^{(1)k2}_{0j2})$$

$$= U + VP\gamma. \tag{2.20}$$

which is used to calculate the UV term in Eq. (2.19). Other terms denoted as . . . in Eq. (2.19) are generated by substituting the indices 1, 2, and 3 in all possible ways, and then by substituting three indices (i_1, i_2, and i_3) in all possible ways. The projector P and the correction to the 1-DM γ is written with the unperturbed first-order density matrix $\Gamma_0^{(1)}$ as

$$P^l_k = 2\Gamma^{(1)l}_{0k} - \delta^l_k, \tag{2.21}$$

$$\gamma^i_j = \Gamma^{(1)i}_{j} - \Gamma^{(1)i}_{0j}, \tag{2.22}$$

where δ^l_k is Kronecker's delta.

By substituting Eq. (2.20) into Eq. (2.19), the UV term $^{UV}\Gamma^{(3)}$ can be written in an infinite sum as

$$^{UV}\Gamma^{(3)} = \frac{1}{6}(UPU + UP\gamma PU + UP\gamma P\gamma PU + \cdots)$$

$$\tag{2.23}$$

Since Eqs. (2.19)–(2.22) do not contain orbital energies, we can use any idempotent first-order density matrices whose N eigenvalues are equal to 1, and the rest are equal to 0 as unperturbed ones (N is the number of electrons). In the calculations below, the HF density matrix is used as an unperturbed one. Once we get the UV term of the 3-DM, the spin-sum yields the 3-RDM in the same way as the 4-RDM.
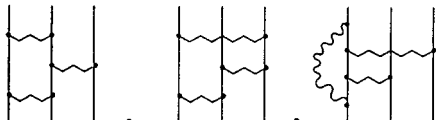
The lowest-order missing term in the present UV approximation is the second-order one, which is attributed to the approximation used in Eq. (2.17): in the last term of Eq. (2.10), we omitted the term with two internal times t and t' being the same sign, $tt' > 0$, because Eqs. (2.15) and (2.16) do not hold in this case. This missing term contributes to the elements $\Gamma^{(3)i1,i2,i3}_{j1,j2,j3}$ with j_{1-3} are occupied and i_{1-3} are unoccupied (or j_{1-3} are unoccupied and i_{1-3} are occupied). By applying standard diagrammatic techniques and integrating the time variables, the missing term is written in an explicit form as

$$\Delta\Gamma^{(3)i1,i2,i3}_{j1,j2,j3} = \frac{1}{6\Delta\epsilon} \sum_{k}^{\text{unoccupied}} \frac{\langle ki_2|V_0|j_1j_2\rangle}{\epsilon_k + \epsilon_{i2} - \epsilon_{j1} - \epsilon_{j2}} \langle i_1 i_3|V_0|kj_3\rangle$$
$$- \frac{1}{6\Delta\epsilon} \sum_{k}^{\text{occupied}} \frac{\langle i_1 i_3|V_0|kj_3\rangle}{\epsilon_{i1} + \epsilon_{i3} - \epsilon_k - \epsilon_{j3}}$$
$$\times \langle ki_2|V_0|j_1j_2\rangle, \qquad (2.24)$$

$$\Delta\epsilon = \epsilon_{i1} + \epsilon_{i2} + \epsilon_{i3} - \epsilon_{j1} - \epsilon_{j2} - \epsilon_{j3},$$

where V_0 is the perturbation operator, the difference between the total Hamiltonian and the Fock operator. We did not include this term in the present calculation, because our aim here is to express the 3-RDM in terms of the 1- and 2-RDM's alone, but this term additionally includes the orbital energies and the perturbation operator. We expect that this term is small because it is proportional to the three-body cluster amplitude in the lowest second order. In addition to the lowest second-order term given by Eq. (2.24), we can include some higher-order terms if we substitute $\pm\langle ki_2|V_0|j_1j_2\rangle/(\epsilon_k + \epsilon_{i2} - \epsilon_{j1} - \epsilon_{j2})$ in Eq. (2.24) with U. In Sec. III we will show the contribution of this term in actual calculations of atoms and molecules.

In the present formulation, we also neglect the third- and higher-order terms which cannot be broken into two parts by cutting an electron propagator, as expressed by

$$(2.25)$$

The physical meaning of the present approximation of the 3-RDM may be explained as follows. The three-particle collision term in the last term of Eq. (2.10) is considered to include two distinct effects: three particles interact at the same time (three-body cluster effect), or particle (hole) 2 interacts with particle 1, moves some distance, then interacts with particle 3. The UV term represents the latter process. Because of the short-range nature of the electron correlations

[14], the three-body cluster effect is relatively small in atoms and molecules, and is neglected in the present approximation.

To test the accuracy of the approximations for the 4- and 3-RDM's given in this section, we calculated the 4-RDM from the exact 1-, 2-, and 3-RDM's, and the 3-RDM from the exact 1- and 2-RDM's for the singlet ground state of Be, and the results were presented in Ref. [11]. Our approximations were very accurate, and reduced the errors of the IPH approximations by about two orders of magnitude for both 3- and 4-RDM's.

III. DIRECT DETERMINATION OF THE DENSITY MATRIX

In Sec. II, we derived a decoupling approximation for the 3- and 4-RDM's whose accuracy is up to about second order of the perturbation. In contrast to the approximation adopted by Valdemoro and co-workers, our approximation involves almost all the second-order perturbation terms, except for the term given by Eq. (2.24). This is necessary for a quantitative description of the electronic structure of atoms and molecules. Although our approximation based on the Green's-function technique is conceptually simple and systematically improvable, the validity of the approximation itself must be checked through numerical calculations. In a previous paper [11] we solved the second-order density equation iteratively using the decoupling approximation of the 3- and 4-RDM's described above.

In this section, we first summarize our calculational method and then give the calculated results. We used the second-order density equation [Eq. (1.1) with $n=2$] in matrix form, which can be represented as

$$R^{i1,i2}_{j1,j2} = ED^{i1,i2}_{j1,j2}, \qquad (3.1)$$

where the density matrix and the energy density matrix are given by

$$D^{i1,i2}_{j1,j2} = \tfrac{1}{2}\langle E^{i1,i2}_{j1,j2}\rangle, \qquad (3.2)$$

$$R^{i1,i2}_{j1,j2} = \tfrac{1}{2}\langle HE^{i1,i2}_{j1,j2}\rangle, \qquad (3.3)$$

$$E^{i1,i2}_{j1,j2} = \sum_{\sigma1,\sigma2} a^{\dagger}_{i1\sigma1} a^{\dagger}_{i2\sigma2} a_{j2\sigma2} a_{j1\sigma1}. \qquad (3.4)$$

The original integrodifferential equation was replaced by the matrix equation including the partial trace. The density matrices and the Hamiltonian were represented in matrices whose one-electron base are the HF orbitals. The generalized two-electron integrals were used for simplicity.

Equation (3.1) is equivalent to the two conditions

$$\frac{1}{2}(R^{i1,i2}_{j1,j2} + R^{j1,j2}_{i1,i2}) - ED^{i1,i2}_{j1,j2} = 0, \qquad (3.5)$$

$$R^{i1,i2}_{j1,j2} - R^{j1,j2}_{i1,i2} = 0 \qquad (3.6)$$

because of the Hermiticity of the 2-RDM,

$$D^{i1,i2}_{j1,j2} = D^{j1,j2}_{i1,i2}. \qquad (3.7)$$

In the present calculation, we used the Hermite part of the density equation, Eq. (3.5), imposing the Hermiticity, Eq. (3.7), and did not use the two-particle Brillouin condition [Eq. (3.6)].

We approximate the 3-RDM from 1- and 2-RDM's, and then 4-RDM from 1-, 2-, and 3-RDM's, using the decoupling approximations given in Sec. II. We then put these 3- and 4-RDM's to Eq. (3.5), and solve it iteratively. Since the present decoupling approximations of the 3- and 4-RDM's are correct essentially up to the second order in the perturbation of the electron correlation, we refer to the present method as DEPT2 (density equation with the 3- and 4-RDM's correct to second-order in correlation perturbation), or simply DE2. In this notation, the solution based on the IPH approximation (original Valdemoro's approximation) may be referred to as DEPT1 or DE1, since the IPH approximation of the 3- and 4-RDM's corresponds to the first-order approximation.

Since the 1-RDM was represented by the 2-RDM, and the 3- and 4-RDM's by the sums of the products of the 1- and 2-RDM's in the present approximation, the density equation in matrix form becomes a multidimensional nonlinear equation. This equation was solved by Newton's method, which is often used for this kind of problem. The iterative procedure is as follows. We use the HF 2-RDM as an initial guess, normalize the trial 2-RDM, then calculate the energy and the 3- and 4-RDM's from the 1- and 2-RDM's, and substitute them into Eq. (3.5). Then we calculate a correction of the 2-RDM (and hence a new 2-RDM) by Newton's method. This procedure is repeated until the convergence is obtained. In some cases, interpolation techniques are useful for an efficient convergence: the previous and present 2-RDM's are averaged with a given weight. We used the symmetry property ($D_{j1,j2}^{i1,i2} = D_{j2,j1}^{i2,i1}$) of the 2-RDM in addition to the Hermiticity to reduce the number of the variables.

We calculate the coefficient matrix of the linear equation in the Newton procedure as follows. From its definition this coefficient matrix is determined using the linearlized density equation. The density equation with the decoupling approximations of the 3- and 4-RDM's contains linear and higher-order terms of the 2-RDM. The coefficient matrix elements derived from the linear term are calculated in every iteration. The rest are calculated using the HF RDM's at the first iteration. For a difficult convergence case, they are calculated at each iteration using the IPH approximations for both 3- and 4-RDM's.

In the previous communication [11] we have applied the DE2 method to several atoms and singly bonded molecules; Be, Ne, H_2O, NH_3, H_3O^+, CH_4, BH_4^-, NH_4^+, and CH_3F, and found that our method shows a good convergence, giving energies as accurate as and density matrices more accurate than the SDCI one. In this paper we apply the DE2 method to more complex systems (better basis sets and larger molecules). New molecules include singly bonded ones (CH_3OH,CH_3NH_2,C_2H_6), and multiply bonded ones (N_2,CO,C_2H_2). Next we give a comparison of the accuracies of the various decoupling approximations from DE1 to DE2: the results of the density-equation method are compared with the full-CI results.

Comparative wave-function calculations were done at the HF, SDCI [16], full-CI [17] (in case of relatively small basis

sets), and fourth-order Møller-Plesset perturbation method (MP4, for larger cases). Experimental molecular geometries [18] were used and some $1s$ core orbitals of C, N, O, and F were frozen.

Tables I and II show the summary of the present results. In Table I we compare the energies and the properties calculated by the present DE2 method with those of the wave-function approaches. The results for the double-ζ basis [19] and the minimal Slater-type-orbital STO-6G basis [20] were grouped separately. The DE2 method includes the UV and 2P terms in the 3- and 4-RDM's, respectively, but does not include the term given by Eq. (2.24).

It is known that the Hartree-Fock theory can be formulated as an equation for the first-order density matrix, and the *uncorrelated*, Hartree-Fock density matrix can be calculated without using the wave function [3,4,12,21]. However, few attempts have been successful for a direct determination of the *correlated* density matrices. The variational method imposing approximate N-representability conditions on the second-order density matrix does not work well, except for some special systems with a very small number of electrons [1,22]. With the use of the nonvariational density-equation method and accurate decoupling approximations, we have been able to determine the *correlated energy* and the *correlated density matrices* of general atoms and molecules quantitatively *without any use of the wave function*. The use of the density equation and the density matrix instead of the the Schrödinger equation and the wave function is the central idea in the present density-equation approach.

As seen in Table I, the energies of the DE2 method are as accurate as and even more accurate than the SDCI results. This is true even for acetylene with double-ζ basis distributing ten electrons within 20 molecular orbitals in the active space. This is the largest calculation ever made using the density equation. The full-CI calculations were difficult for this class of systems, so that the comparison was made with the MP4 results. Because of the limitation of our current program, we did not apply this method to larger molecules and to larger active spaces, but this limitation should be overcome. The calculated dipole moment of the CO molecule by the DE2 method was 0.0344 a.u., which agrees well with the SDTQ (single, double, triple, and quadruple)-CI value, 0.0445 a.u., and the experiment, 0.044 a.u. [23]. The calculated rotational barrier of ethane was 3.31 kcal/mol, which also agrees well with the MP4 value, 3.34 kcal/mol, and the experiment, 2.9 kcal/mol [24].

Even though the energy errors shown in Table I are sometimes larger than those of the SDCI method, the dipole or quadrupole moments calculated from the present density matrices, are more accurate than those of the SDCI method. This result is understood from the facts that the density-equation method is a nonvariational method while the SDCI method is a variational one, and that the density-equation method is a method directly solving the densities themselves.

In Table II we compare the calculated energies and density matrices obtained by the various decoupling approximations of the 3- and 4-RDM's from the DE1 to the DE2 level. The effects of the term given by Eq. (2.24) are further investigated. It gives more detailed information than that given in

TABLE I. Energies and properties calculated by the density-equation method and the wave-function method.

Molecule	Density equation	Wave function		
	DE2[a]	Hartree-Fock	SDCI	Full-CI[b]
Active Number of space, electrons[c]	Energy in a.u. (correlation energy error in percentage) dipole or quadrupole moment in a.u.[d]			
Double-ζ basis (Ref. [19])				
H_2O	$-76.148\,27(6.48)$	$-76.009\,84(100)$	$-76.150\,01(5.30)$	$-76.157\,87(0)$
5×9, 10	0.9801	1.0142	0.9826	0.9762
NH_3	$-56.298\,88(4.24)$	$-56.175\,99(100)$	$-56.297\,17(5.58)$	$-56.304\,33(0)$
4×10, 8	0.9098	0.9226	0.9133	0.9081
CH_4	$-40.295\,82(3.73)$	$-40.185\,46(100)$	$-40.294\,05(5.27)$	$-40.300\,09(0)$
4×12, 8	0	0	0	0
HF	$-100.218\,76(2.85)$	$-100.021\,79(100)$	$-100.216\,22(4.10)$	$-100.224\,53(0)$
4×12, 8	0.7920	0.8215	0.7931	0.7919
N_2	$-109.079\,09(12.27)^e$	$-108.878\,26(100)$	$-109.082\,19(10.92)^e$	$-109.107\,19^e(0)$
5×11, 10	2.046	1.808	1.993	2.054^f
CO	$-112.872\,93(12.99)^e$	$-112.685\,05(100)$	$-112.873\,82(12.58)^e$	$-112.900\,98^e(0)$
5×11, 10	0.0344	-0.1652	0.0586	0.0445^f
C_2H_2	$-76.980\,06(6.37)^e$	$-76.799\,07(100)$	$-76.975\,59(8.65)^e$	$-76.992\,30^e(0)$
5×15, 10	4.642	5.315	4.817	4.762^g
STO-6G basis (Ref. [20])				
CH_3OH	$-114.711\,44(5.24)$	$-114.589\,82(100)$	$-114.710\,82(5.72)$	$-114.718\,16(0)$
7×5, 14	0.6024	0.6548	0.6058	0.5991
CH_3NH_2	$-95.067\,81(3.76)$	$-94.938\,49(100)$	$-95.065\,05(5.81)$	$-95.072\,86(0)$
7×6, 14	0.5634	0.5754	0.5633	0.5619
C_2H_6 (staggered)	$-79.209\,24(0.24)^e$	$-79.062\,33(100)$	$-79.204\,48(3.47)^e$	$-79.209\,59^e(0)$
7×7, 14	0.4279	0.4589	0.4307	0.4284^f
C_2H_6 (eclipsed)	$-79.204\,05(0.20)^e$	$-79.056\,86(100)$	$-79.199\,25(3.46)^e$	$-79.204\,35^e(0)$
7×7, 14	0.4843	0.5159	0.4876	0.4851^f

[a]The UV and $2P$ terms in the 3- and 4-RDM's, respectively, are included.
[b]Full-CI only for small active space calculations.
[c]Number of electrons in the active space.
[d]Quadrupole moment is given in case of zero dipole moment.
[e]Fourth-order Møller-Plesset values.
[f]SDTQ-CI values.
[g]SDT-CI value.

Ref. [11]. We used the double-ζ STO basis [25] expanded by six Gaussian-type orbitals for Be, and the minimal STO-6G basis [20] for molecules.

We see that unless both of the UV and 2P terms are included in the 3- and 4-RDM's (DE2), the results are not satisfactory. When both terms are included, the convergence of the iterative calculation is remarkably improved, giving satisfactory results for both energy and density matrices in comparison with the full-CI results. Original Valdemoro's approximation (IPH, IPH): DE1 and other combinations $(+UV$, IPH) and (IPH, $+2P$) did not give good results, and did not even converge in some cases. The combinations of (IPH, IPH) and (IPH, $+2P$) give only small fractions of the correlation energies for molecules, as well as too large a correlation energy, twice as large as the exact value for Be, and the density errors are as large as those of the Hartree-Fock method. The combination $(+UV$, IPH), which contains the first, second, and the third terms of Eq. (2.5) for the 4-RDM, gives better results than the above ones. It actually gives the best energies among the density-equation method for NH_4^+ and CO, but it does not give the best densities: the density errors in the $(+UV$, $+2P$): DE2 approximation are smallest in both density-equation and wave-function methods.

Strictly speaking, the DE2 method must be called, say, DE1.9, because it does not include all the second-order terms, and the term given by Eq. (2.24) is missing. We then consider the effect of this term. When this term is further included, and hence the method is strictly DE2, the energy becomes slightly better than that of the DE1.9 method (which is written in Table II as DE2). For the CO molecule the missing term improves the energy considerably, and reduces the correlation energy error up to half of that of DE1.9. However this may be a special case because the effect of the same term is small for the triply bonded molecules N_2 and C_2H_2. In all cases, the density matrices calculated by including the missing term are similar or a bit worse than those calculated by the DE1.9 method.

TABLE II. Comparison of the density-equation method using the various decoupling approximations and the wave-function method. Numbers in square brackets indicate powers of 10.

	Density-equation method					Wave function method		
	DE1		DE2			Hartree-Fock	SDCI	Full-CI
^3D	IPH	$+UV$	IPH	$+UV$	$+UV+$Eq. (2.24)			
^4D	IPH	IPH	$+2P$	$+2P$	$+2P$			
System Active space electrons[a]				Energy Correlation energy error in percentage ^2D error[b]				
Be	$-14.597\,75$	$-14.581\,85$	$-14.598\,50$	$-14.582\,69$	$-14.582\,69$	$-14.568\,53$	$-14.582\,69$	$-14.582\,69$
2×2	-106.4	5.93	-111.6	0.014	$-4.60[-3]$	100	0.028	0
4	$1.165[-2]$	$8.768[-4]$	$1.195[-2]$	$4.823[-5]$	$4.784[-5]$	$4.631[-2]$	$1.141[-4]$	0
H_2O	not conv.	$-75.722\,69$	not conv.	$-75.727\,51$	$-75.727\,70$	$-75.678\,84$	$-75.728\,29$	$-75.729\,02$
5×2		12.6		3.00	2.63	100	1.44	0
10		$9.132[-2]$		$7.122[-3]$	$1.254[-2]$	$3.154[-1]$	$1.030[-2]$	0
CH_4	$-40.124\,26$	$-40.185\,37$	$-40.111\,36$	$-40.187\,26$	$-40.187\,53$	$-40.110\,15$	$-40.187\,72$	$-40.190\,49$
4×4	82.4	6.38	98.5	4.02	3.68	100	3.45	0
8	$2.948[-1]$	$3.818[-2]$	$3.713[-1]$	$9.757[-3]$	$1.007[-2]$	$3.702[-1]$	$2.819[-2]$	0
NH_4^+	$-56.423\,54$	$-56.485\,93$	$-56.404\,41$	$-56.479\,90$	$-56.480\,46$	$-56.400\,47$	$-56.480\,87$	$-56.483\,47$
4×4	72.2	-2.96	95.3	4.31	3.63	100	3.14	0
8	$2.912[-1]$	$4.956[-2]$	$3.394[-1]$	$1.164[-2]$	$1.338[-2]$	$3.671[-1]$	$2.757[-2]$	0
N_2	not conv.	not conv.	not conv.	$-108.673\,19$	$-108.676\,16$	$-108.541\,77$	$-108.687\,46$	$-108.700\,11$
5×3				17.00	15.13	100	7.99	0
10				$7.601[-2]$	$7.106[-2]$	$7.159[-1]$	$1.282[-1]$	0
CO	not conv.	$-112.445\,29$	not conv.	$-112.419\,26$	$-112.431\,25$	$-112.303\,32$	$-112.430\,00$	$-112.442\,61$
5×3		1.93		16.77	8.15	100	9.05	0
10		$3.959[-1]$		$1.202[-1]$	$3.398[-1]$	$7.454[-1]$	$1.618[-1]$	0
C_2H_2	not conv.	$-76.752\,13$	not conv.	$-76.757\,17$	$-76.758\,28$	$-76.603\,02$	$-76.760\,57$	$-76.776\,19$
5×5		14.307		10.98	10.34	100	9.02	0
10		$1.852[-1]$		$6.493[-2]$	$6.353[-2]$	$8.864[-1]$	$1.711[-1]$	0

[a]Number of electrons in the active space.
[b]Square norm of the difference between the calculated 2-RDM and the full-CI one.

It is remarkable that the correlation energy errors of the present density-equation method are improved as the system becomes larger (in size and in basis set). This is seen by comparing the results given in Table I with those of Table II, the former being for larger systems. Though the energy errors of the density-equation method given in Table II are almost always worse than those of the SDCI method, those in Table I are opposite except for H_2O, N_2, and CO. This is certainly an encouraging result for the density-equation method.

Recently, Colmenero and Valdemoro applied the density equation, using their approximations for 3- and 4-RDM's, to four-electron systems like Be, B^+, etc. and a six-electron system Betta [10]. They further used corrections adopting the 3-RDM spin-symmetry, and keeping some diagonal elements of the 3-RDM non-negative. The error in the correlation energy for Be was 0.27%, which is comparable to our present result, showing that their additional corrections worked well.

In our calculations, some diagonal elements of the approximate 3-RDM were slightly negative, though they must be non-negative for the N-representable one. Hence we further tried to keep all the diagonal elements of the 3-RDM and 3-HRDM non-negative, and at the same time to keep them spin symmetry adapted. The spin symmetry of the

RDM corresponds to the permutational antisymmetry of the explicit (unintegrated) variables of the DM. Our correction used here is similar to the one used by Valdemoro and co-workers [8]: if a negative diagonal element appeared in the 3-RDM, it was corrected to be zero, and some nondiagonal elements were modified to keep the spin symmetry. Similar corrections were applied to the 3-HRDM because the 3-RDM and the 3-HRDM must satisfy an exact relation [8]. However, these corrections either had no effect or resulted in a divergence at least from our simple convergence technique. Hence we did not use them in the calculations given in Tables I and II. Although these corrections keep the spin symmetry of the 3-RDM and hence the antisymmetry of the *explicit* variables of the 3-DM, it may not ensure the antisymmetry of the *integrated* variables of the 3-DM.

We next show the convergence property of our method. Figure 1 shows the energy, the errors in the density equation, and the 2-RDM for each iteration of the calculation of CH_3F. The error in the density equation means the square norm of the difference between the rhs and lhs of the density equation, and the error in the 2-RDM means the square norm of the difference between the calculated 2-RDM and the exact one. We see that our iterative method gave a nice convergence which requires about ten iterations, in contrast to
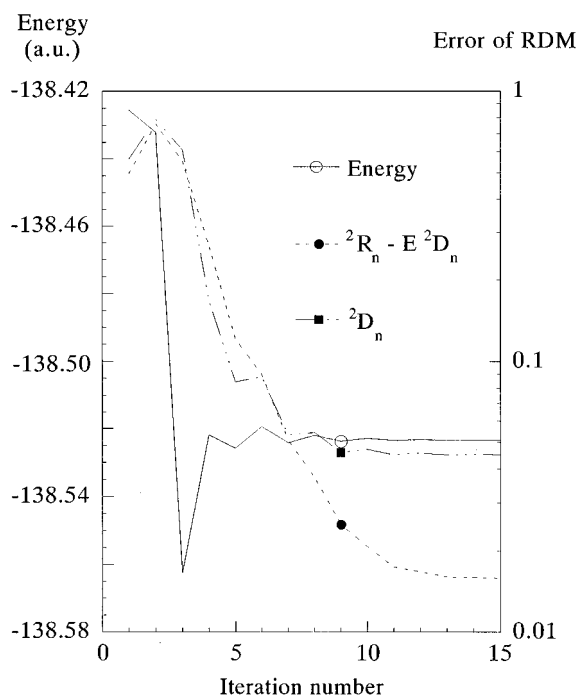
FIG. 1. Energy and errors of the density equation and 2-RDM for each iteration of the calculation of CH_3F.

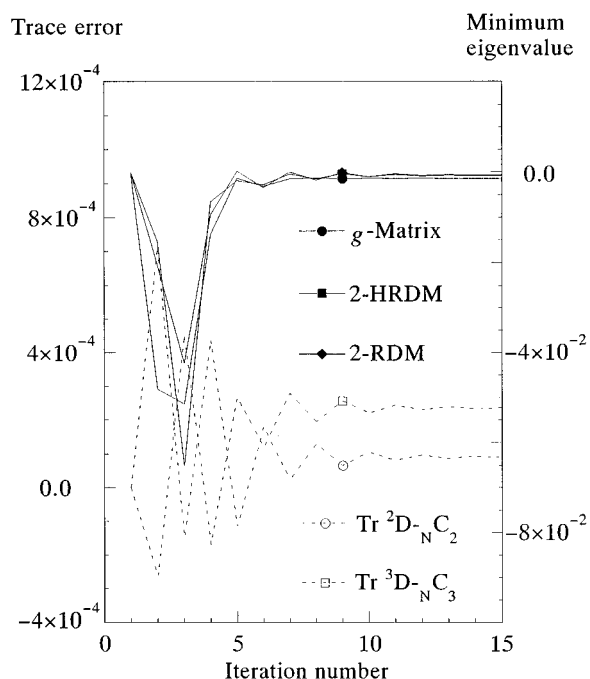

FIG. 2. Minimum eigenvalues of the 2-RDM and 2-HRDM, and g matrix and trace errors of the n-RDM's for each iteration of the calculation of CH_3F.

the previous one [10] which required longer iterations.

We examine the N representability of the calculated 2-RDM. We calculated some necessary requirements, the P, Q, and G conditions [1,2], which are the non-negativities of the RDM, HRDM, and the g matrix defined as

$$g_{ij,kl} = 2 \times {}^2D_{il}^{jk} + \delta_i^k \, {}^1D_l^j - {}^1D_i^j \, {}^1D_l^k. \quad (3.8)$$

The G condition is equivalent to the non-negativity of the norm,

$$\langle B^\dagger B \rangle = x_{ij}^* x_{kl} g_{ij,kl} \geq 0, \quad (3.9)$$

in which x_{ij} are arbitrary scalars and B is the operator defined as

$$B = \sum_{ij,\sigma} x_{ij}(a_{i\sigma}^\dagger a_{j\sigma} - {}^1D_j^i). \quad (3.10)$$

Table III shows the lowest eigenvalues of the three matri-

ces P, Q, and g for several molecules. Though they must be non-negative for the N-representable 2-RDM's, the lowest values are slightly negative but the absolute values are small. Note that the sums of the eigenvalues of the P and Q matrices are quite large, which are ${}_NC_2$ and ${}_MC_2$, respectively, where N being the number of the electrons and M the number of the holes. Note also that the sum of the eigenvalues of the g matrix in the Hartree-Fock approximation is $N(N+2M)/2$, which is also quite large. Figure 2 shows these lowest eigenvalues for each iteration of the calculation of CH_3F. The deviations from zero are large in the first few iterations, but become very small after convergence, that is, the calculated 2-RDM's *almost* satisfy these three conditions. A small deviation from the exact N representability is due to an inaccuracy of our decoupling approximation of the RDM's. As the approximation becomes more accurate, the calculated 2-RDM's should satisfy the N-representability condition more precisely. Figure 2 also shows the trace er-

TABLE III. Minimum eigenvalues of the 2-RDM, 2-HRDM, and g matrix, and the range of the eigenvalues of 1-RDM calculated by the DE2 method. Numbers or square brackets indicate powers of 10.

Molecule	Active space	Number of electrons[a]	2-RDM	2-HRDM	g matrix	1-RDM
H_2O	5×9	10	$-3.34[-4]$	$-1.85[-4]$	$-3.28[-4]$	$1.94[-4] \sim 1.9998$
NH_3	4×10	8	$-4.59[-4]$	$-1.46[-4]$	$-2.70[-4]$	$3.00[-4] \sim 1.9838$
CH_4	4×12	8	$-5.71[-4]$	$-1.59[-4]$	$-3.22[-4]$	$2.35[-4] \sim 1.9815$
CH_3OH	7×5	14	$-5.39[-4]$	$-4.35[-4]$	$-5.39[-4]$	$1.78[-2] \sim 1.9974$
N_2	5×11	10	$-1.02[-3]$	$-5.31[-4]$	$-3.70[-3]$	$4.30[-4] \sim 1.9866$
CO	5×11	10	$-7.83[-4]$	$-3.37[-4]$	$-6.40[-3]$	$5.51[-4] \sim 1.9884$
C_2H_2	5×15	10	$-1.52[-3]$	$-5.94[-4]$	$-3.10[-3]$	$3.40[-5] \sim 1.9796$

[a]Number of electrons in the active space.

rors of the n-RDM from the exact trace, $_NC_n$, which also became very small after the convergence.

We finally check the N representability of the 1-RDM's. The necessary and sufficient N-representability condition for the 1-RDM is that all the eigenvalues are in the range of zero to two [2]. Table III shows the range of the eigenvalues of the 1-RDM's for several molecules. All the eigenvalues of the calculated 1-RDM's are in the range of zero to two, showing that the calculated 1-RDM's are exactly N representable. This was true for all atoms and molecules calculated by the present DE2 method.

IV. CONCLUSION

The second-order density matrices of some atoms and molecules were directly calculated without any use of the wave function. We solved the density equation using the decoupling approximations for the third- and fourth-order density matrices. The decoupling approximations were derived based on the Green's-function technique and using the Feynman diagram. Previous approximations by Valdemoro and co-workers [7,8] were derived as a special case. The present approximation involves up to the second-order and some higher-order perturbation terms in electron correlations, and is more accurate than the previous one [7,8], which neglects some important second-order terms. The calculated 2-RDM's were more accurate than the SDCI results, and the calculated energies were comparable with or better than the SDCI ones: the SDCI method is a variational method which minimize the energy, while the density-equation method is a nonvariational method directly determining the 2-RDM. The density-equation method is found to give better quality results as the system becomes larger. The convergence was fairly good and the calculated 2-RDM's almost satisfied some necessary conditions of the N-representability, P, Q, and G conditions, while the 1-RDM's were exactly N representable. These results show that the density-equation method is very promising.

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