Direct Determination of the Quantum-Mechanical Density Matrix Using the Density Equation

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With the use of the density equation [H. Nakatsuji, Phys. Rev. A **14**, 41 (1976)], the second-order density matrices are directly determined without any use of the wave functions. The third- and fourth-order reduced density matrices (RDM's) are decoupled into lower-order ones using the Green's function technique. This method is applied to Be, Ne, H_2O, H_3O^+, NH_3, CH_4, BH_4^-, NH_4^+, and CH_3F, and the results are successfully compared with the full configuration interaction results. The convergence is fairly good, and the calculated second-order RDM's almost satisfy the necessary conditions of the N representability, the P, Q, and G conditions, and the first-order RDM's are exactly N representable. These results show that the present method is very promising.

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It is known that the many-electron wave function involves more information than we need to know. Therefore the determination of density or density matrices without using the wave function could be a convenient alternative to wave mechanics, and along this line the density functional theories [1,2] and density matrix approaches [3], etc., have been presented.

The Hohenberg-Kohn theorem [1] ensures the use of the electron density as a basic variable. Recently, this density functional theory has been much developed and widely used [1,2]. However, the Hohenberg-Kohn theorem is an existence theorem, and the explicit functional form is still not known [4].

All of the important physical quantities are obtained from the second-order density matrix. Since it determines the energy, we can apply the variational principle in a suitable domain of the density matrices [3]. However, it is still not completely known what conditions the Pauli principle enforces on the density matrices (N representability condition) [5]. Moreover, since these conditions may be very complicated, it is impracticable to carry out such variational calculations.

On the other hand, a nonvariational approach for the direct determination of the density matrix has been proposed by one of the present authors [6]. He showed that the equation

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

(1)

which is called the density equation, is equivalent to the Schrödinger equation for *each* n with $n \geq 2$. That is, this equation in the domain of the N-representable density matrices is the necessary and sufficient condition for the corresponding wave function to satisfy the Schrödinger equation. The necessity alone was shown by Cho [7] and by Cohen and Frishberg [8]. However, unless the N representability condition is not known, the number of unknowns exceeds the number of conditions [9], since the nth-order density equation contains nth-, $(n+1)$th, and $(n+2)$th-order density matrices. On the other hand, if we can calculate in some way or even approximately the $(n+1)$th and $(n+2)$th-order density matrices from the nth- and lower-order ones, it becomes possible to solve the density equation and calculate the density matrix directly without any use of the wave function. The purpose of this communication is to show that such a method is now almost established.

Recently, Valdemoro *et al.* have suggested a decoupling approximation of the higher-order density matrices

in terms of the lower-order ones, based essentially on the fermion's anticommutation relations [10], and Colmenero and Valdemoro applied it, using the density equation, to some four-electron systems [11]. However, as we shall show later, this method seems to have limitations for more complex atoms and molecules. We have derived more accurate decoupling approximations of the third- and fourth-order density matrices in terms of the lower-order ones using the Green's function technique, and applied them, using the density equation, to some atoms and molecules. In this communication we briefly outline the method and give the results of the calculations, comparing them with the traditional wave function approach. We actually use the second-order density equation ($n = 2$).

The density matrix (DM) $\Gamma^{(n)}$ is related to the Green's function $G^{(n)}$ as

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

and the reduced density matrix (RDM) ^nD is defined by

$$^nD(r'_1 \cdots r'_n | r_1 \cdots r_n) = \sum_{\sigma_1 \cdots \sigma_n} \Gamma^{(n)}(x'_1 \cdots x'_n | x_1 \cdots x_n),$$

where σ_i is a spin variable. Taking lower-order perturbation series of the Green's functions, we introduce the following decoupling approximations for the third- and fourth-order Green's functions:

$$G^{(3)} = \quad | \; | \; | \quad + \quad \vcenter{\hbox{$\rightthreetimes$}}| \quad + \quad \vcenter{\hbox{$\rightthreetimes$}} \qquad (2)$$

$$G^{(4)} = \quad | \; | \; | \; | \quad + \quad \vcenter{\hbox{$\rightthreetimes$}}| \; | \quad + \quad \vcenter{\hbox{$\rightthreetimes$}}| \quad + \quad \vcenter{\hbox{$\rightthreetimes\rightthreetimes$}} . \qquad (3)$$

In Eqs. (2) and (3), we give only the representative graphs, but we include all the related terms including the exchange terms. The first two terms of Eq. (2) and the first three terms of Eq. (3) are the same as those given by Valdemoro *et al.,* and correspond approximately to the first-order terms. The last terms of Eqs. (2) and (3), which we call *UV* and 2P (two-pair) terms, respectively, are the second-order terms in electron correlations. These terms are more explicitly given below, and their physical meanings are clarified.

First we define the collision term U by

$$U(x'_1 x'_2 | x_1 x_2) - U(x'_1 x'_2 | x_2 x_1) = 2\Gamma^{(2)}(x'_1 x'_2 | x_1 x_2)$$
$$- \begin{vmatrix} \Gamma^{(1)}(x'_1|x_1)\Gamma^{(1)}(x'_1|x_2) \\ \Gamma^{(1)}(x'_2|x_1)\Gamma^{(1)}(x'_2|x_2) \end{vmatrix},$$
$$(4)$$

where the second term in the rhs is the second-order DM (2-DM) in the independent-particle approximation [2,6]. The 2P term in the 4-DM is defined by

$$^{2P}\Gamma^{(4)\,i1,i2,i3,i4}_{\qquad j1,j2,j3,j4} = \frac{1}{24} U^{i1,i2}_{j1,j2} U^{i3,i4}_{j3,j4} + \cdots,$$

where the sum is for all the permuted, antisymmetrized products of U and consists of 72 terms.

The *UV* term in the 3-DM is defined by

$$^{UV}\Gamma^{(3)\,i1,i2,i3}_{\qquad j1,j2,j3} = \frac{1}{6} \left(\sum_k^{\text{occupied}} - \sum_k^{\text{virtual}} \right) \left(U^{i1,k}_{j1,j2} V^{i2,i3}_{k,j3} + \cdots \right).$$

The U term is defined by Eq. (4), and the V term is the solution of the linear equation

$$V^{i1,i2}_{j1,j2} = U^{i1,i2}_{j1,j2} + \left(\sum_k^{\text{occupied}} - \sum_k^{\text{virtual}} \right) V^{i1,i2}_{j1,k} \left(\Gamma^{(1)k}_{j2} - \Gamma^{(1)k}_{\text{HF}j2} \right),$$

where HF stands for Hartree-Fock. The *UV* term represents the following process: A particle (or a hole) 2 first collides with 1 ($U^{i1,k}_{j1,j2}$), moves some distance, then collides with 3 ($V^{i2,i3}_{k,j3}$). The sum of all the intermediate states k yields the total amplitude, and the sign reflects whether a particle or a hole propagates as an intermediate state. The second term of the linear equation represents the subtraction of some overcounted diagrams. Note that *UV* term is not the simple product of the lower-order density matrices.

Since the Green's function method is quite general, Valdemoro's decoupling approximation was derived as a special case. Valdemoro's procedure, which is quite interesting, is based on the exact relation between the n-RDM's ^nD and the n-hole RDM's (n-HRDM's) $^n\overline{D}$, for example,

$$\overline{D}^{j1,j2}_{i1,i2} - D^{i1,i2}_{j1,j2} = \tfrac{1}{2} \left(\overline{D}^{j1}_{i1} \overline{D}^{j2}_{i2} - \tfrac{1}{2} \overline{D}^{j2}_{i1} \overline{D}^{j1}_{i2} \right)$$
$$- \tfrac{1}{2} \left(D^{i1}_{j1} D^{i2}_{j2} - \tfrac{1}{2} D^{i2}_{j1} D^{i1}_{j2} \right).$$

Valdemoro *et al.* put the RDM (HRDM) term in the left-hand side to be equal to the RDM (HRDM) terms on the right-hand side. Hence this approximation has the possibility of neglecting some terms that are common to both RDM and HRDM. In addition, their approximation represents the higher-order RDM's by the simple products of the lower-order ones, which is generally impossible.

TABLE I.   Errors of the various approximations of the 3- and 4-RDM's for the ground state of Be.

3-RDM				4-RDM			
Element[a] j_{123}, m_{123}	Valdemoro error	+*UV* error	Full-CI value	Element[a] j_{1234}, m_{1234}	Valdemoro error	+2P error	Full-CI value
2,3,3,2,3,3	3.356×10^{-4}	7.250×10^{-7}	1.758×10^{-4}	3,3,2,2,3,3,2,2	-7.928×10^{-5}	2.931×10^{-7}	3.933×10^{-5}
2,2,3,2,2,3	-3.174×10^{-4}	-4.751×10^{-7}	2.029×10^{-4}	3,3,2,2,3,3,1,1	-5.581×10^{-5}	1.169×10^{-7}	5.591×10^{-5}
2,2,3,1,1,3	-2.233×10^{-4}	-2.552×10^{-7}	2.235×10^{-4}	3,3,2,2,2,3,2,3	3.964×10^{-5}	-1.466×10^{-7}	-1.967×10^{-5}
1,1,3,1,1,3	-2.015×10^{-4}	-2.814×10^{-7}	3.187×10^{-4}	3,3,1,1,3,3,1,1	-3.922×10^{-5}	1.779×10^{-7}	7.948×10^{-5}
1,3,3,1,3,3	1.752×10^{-4}	4.459×10^{-7}	3.364×10^{-4}	4,4,2,2,3,3,1,1	-3.740×10^{-5}	1.869×10^{-8}	3.742×10^{-5}
3,3,2,2,3,3	-1.678×10^{-4}	-3.625×10^{-7}	-8.789×10^{-5}	4,4,3,3,2,2,1,1	-3.652×10^{-5}	-1.731×10^{-7}	3.657×10^{-5}
3,2,2,2,2,3	1.587×10^{-4}	2.376×10^{-7}	-1.014×10^{-4}	4,3,2,2,3,3,1,1	2.973×10^{-5}	-3.329×10^{-8}	-2.977×10^{-5}
				3,3,2,1,3,1,3	2.791×10^{-5}	-5.844×10^{-8}	-2.796×10^{-5}
				4,4,1,1,3,3,1,1	-2.628×10^{-5}	6.203×10^{-8}	1.631×10^{-6}

[a]All the 3- and 4-RDM elements with the Valdemoro errors larger than 1.5×10^{-4} and 2.5×10^{-5}, respectively, are listed.

TABLE II. Calculated energies and density errors in the density-equation method and the wave function approach.

System	Active space Number of electrons	Density-equation method		Wave function approach		
		Valdemoro	present[a]	Hartree-Fock	SDCI	Full-CI
		Energy correlation energy error(%)[b] ^2D error[c]				
Be	2×2	-14.59775	-14.58269	-14.56853	-14.58269	-14.58269
	4	-106.4	0.014	100	0.028	0
		1.165×10^{-2}	4.823×10^{-5}	4.631×10^{-2}	1.141×10^{-4}	0
Ne	3×6	not conv.	128.57862	-128.49637	-128.57726	-128.57835
	6		-0.331	100	1.33	0
			1.373×10^{-2}	1.947×10^{-1}	6.943×10^{-3}	0
H_2O	5×2	not conv.	-76.72751	-75.67884	-75.72829	-75.72902
	10		3.00	100	1.44	0
			7.122×10^{-3}	3.154×10^{-1}	1.030×10^{-2}	0
NH_3	5×3	not conv.	-56.05293	-55.98860	-56.05344	-56.05513
	10		3.30	100	2.53	0
			6.231×10^{-3}	3.473×10^{-1}	2.039×10^{-2}	0
H_3O^+	5×3	not conv.	-76.09629	-76.03996	-76.09706	-76.09833
	10		3.55	100	2.18	0
			9.977×10^{-3}	3.067×10^{-1}	1.793×10^{-2}	0
CH_4	4×4	-40.12426	-40.18726	-40.11015	-40.18772	-40.19049
	8	82.4	4.02	100	3.45	0
		2.948×10^{-1}	9.757×10^{-3}	3.702×10^{-1}	2.819×10^{-2}	0
BH_4^-	4×4	-26.80563	-26.87450	-26.80526	-26.87534	-26.87719
	8	99.5	3.75	100	2.58	0
		3.198×10^{-1}	1.072×10^{-2}	3.813×10^{-1}	2.831×10^{-2}	0
NH_4^+	4×4	-56.42354	-56.47990	-56.40047	-56.48087	-56.48347
	8	72.2	4.31	100	3.14	0
		2.912×10^{-1}	1.164×10^{-2}	3.671×10^{-1}	2.757×10^{-2}	0
CH_3F	7×4	not conv.	-139.52339	-138.42548	-138.52491	-138.53004
	11		6.37	100	4.91	0
			4.514×10^{-2}	5.614×10^{-1}	6.118×10^{-2}	0

[a]Present approximation corresponds to Valdemoro +UV for 3-RDM and Valdemoro +2P for 4-RDM.
[b]Error percentage in the correlation energy.
[c]This error means the square norm of the differences between the calculated 2-RDM and the full-CI one.

Note that we have shown previously [6] that, by putting the independent particle model approximation

$$D_{j1,j2}^{i1,i2} = \frac{1}{2}\left(D_{j1}^{i1} D_{j2}^{i2} - \frac{1}{2} D_{j1}^{i2} D_{j2}^{i1} \right)$$

into the density equation, we get the HF equation as a result.

Based on the above decoupling approximation of the 3- and 4-RDM's, we solved the second-order density equation [Eq. (1) with $n = 2$] iteratively. The HF orbitals were used as one-electron basis and the HF 2-RDM was used as an initial guess. The iterative procedure is as follows: We first symmetrize and normalize a trial 2-RDM, then calculate the energy and the 3- and 4-RDM's from the 2-RDM, and substitute them in the density equation. Since only the exact density matrices satisfy it, its right-hand side will differ from the left-hand side in general. From this residue we calculate a new 2-RDM by the Newton method. The above procedure is repeated until convergence is obtained. In some cases, interpolation techniques are necessary for an efficient convergence: The previous and the present 2-RDM's are averaged with some given weight.

We applied the present density-equation method to several atoms and molecules: Be, Ne, H_2O, H_3O^+, NH_3, CH_4, BH_4^-, NH_4^+, and CH_3F. The comparative wave function approach was used at the HF, configuration-interaction SDCI, and full CI levels. The following basis sets were used: For atoms, the double-zeta Slater-type orbitals (STO's) [12] were used and expanded by six Gaussian-type orbitals (GTO's) [13]. For molecules, the minimal STO-6G basis [13] and the experimental molecular geometries [14] were used. The $1s$ and $2s$ orbitals of Ne and the $1s$ orbitals of CH_4, BH_4^-, NH_4^+, and CH_3F were frozen as cores.

First, we examine the accuracy of the present decoupling approximations as given by Eqs. (2) and (3). We calculated the 3-RDM from the exact 1- and 2-RDM's

and the 4-RDM from the exact 1-, 2-, and 3-RDM's. The exact RDM's were calculated from the full CI wave function. Table I shows the results for Be. In going from Valdemoro's approximation to the present one, the errors are reduced from the order of 10^{-4} to 10^{-7} for the 3-RDM, and from the order of 10^{-5} to 10^{-7} for the 4-RDM. Thus our approximations significantly improve the Valdemoro's ones.

We next compare the results of the density-equation method at different levels of approximations. Table II shows the results of the energies and the 2-RDM's for the calculated systems. In comparison with the exact full CI results, the Valdemoro's approximation shows poor results, while our approximations for the 3- and 4-RDM's improve over it remarkably. Some calculations with the Valdemoro's approximation were difficult to converge, while our approximation led to convergence within a few iterations.

Recently, Colmenero and Valdemoro have applied the density equation, using the Valdemoro's approximations for the 3- and 4-RDM's, to four-electron systems like Be, B^+, etc. [11]. They further used corrections making the RDM's spin-symmetry adapted and keeping the diagonal elements nonnegative. The error in the correlation energy for Be was 0.27%, which is comparable to our $+UV + 2P$ term result. Their special corrections seem to work well for the four-electron atoms. Note, however, that for four-electron systems the 4-RDM is essentially equal to the wave function itself.

On the other hand, our method including the UV and 2P terms works well even for many-electron systems having more than four electrons. This is in marked contrast to the Valdemoro's approximation which either gives very poor results or does not even give a convergence in the calculations. For atoms, the error in the correlation energy is only 0.014% for Be and -0.33% for Ne (the minus sign means overshooting). For molecules, it is 3–4 % for hydrides and 6% for CH_3F. Although these energy errors are larger than those of the SDCI method except for the atoms, the errors of the 2-RDM's measured by the square norms of the deviations from the exact ones are smaller by an order of magnitude than those of the SDCI method. We interpret this as follows: The SDCI method is a variational method, while the present density-equation method is a nonvariational method directly calculating the 2-RDM's.

We finally checked the N representability of the calculated 2-RDM's using some necessary conditions, P, Q, and G conditions [5], which are the nonnegatives of the RDM, the HRDM, and the G matrix. We found that our 2-RDM's almost satisfy these N representability conditions. We also found that all the eigenvalues of the 1-RDM's are in the range of zero to 2, so that the calculated 1-RDM's are exactly N representable [15].

The present study is summarized as follows. With the use of the density equation the second-order density matrices were directly determined without any use of the wave function. The 3- and 4-RDM's were decoupled into lower-order ones using the Green's function technique. The results for the atoms and molecules, Be, Ne, H_2O, H_3O^+, NH_3, CH_4, BH_4^-, NH_4^+, and CH_3F were quite accurate and promising. The convergence was fairly good, and the calculated 2-RDM's almost satisfy some necessary conditions of N representability, while the 1-RDM's are exactly N representable. These results show this method to be very promising. We are now exploring both more accurate and more efficient methods. More details of the theory and the calculations will be published in near future.

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