Chapter 5

Density Equation Theory in Chemical Physics

Hiroshi Nakatsuji
Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606, Japan

1. INTRODUCTION AND DEFINITIONS

Two basic principles in non-relativistic quantum mechanics are the Schrödinger equation (SE),

$$\hat{H}(1,...,N)\,\Psi(1,...,N) = E\,\Psi(1,...,N)\,, \tag{1.1}$$

and the Pauli principle,

$$\hat{P}\,\Psi(1,...,N) = (-)^P\,\Psi(1,...,N)\,, \tag{1.2}$$

[note that the notation $1 \equiv (r_1,\sigma_1)$ is used here and in the following]. The SE is a determinative equation of the wave function Ψ and the Pauli principle imposes an anti-symmetric constraint on Ψ. The wave function depends on all the N electron coordinates of the system, while the Hamiltonian,

$$\hat{H}(1,...,N) = \sum_i^N \hat{v}(i) + \sum_{i>j}^N \hat{w}(i,j)\,, \tag{1.3}$$

is the sum of the one- and two-electron operators, $\hat{v}$ and $\hat{w}$, respectively.

It is generally true that all the elementary physical operators of this universe are written with the sum of the one- and/or two-particle operators: they

never include three and more particle interactions. This fact implies that any physical property can be evaluated from the second-order reduced density matrix (2-RDM) defined by

$$\Gamma_2(1',2';1,2) = \binom{N}{2} \int \Psi^*(1',2',3,...,N) \, \Psi(1,2,3,...,N) \, dx_3...dx_N . \quad (1.4)$$

The reduced density matrices (RDMs) were first introduced by Husimi [1] and developed in particular by Löwdin [2], McWeeny [3], and Davidson [4]. We can calculate electron density $\rho_1(r)$ as a spin sum of the diagonal element of the first-order reduced density matrix (1-RDM) given by

$$\Gamma_1(1';1) = \frac{2}{N-1} \int \Gamma_2(1',2;1,2) \, dx_2 . \quad (1.5)$$

The force $\mathbf{F}_A$ acting on a nucleus A, which is a very important quantity for studying molecular structure and chemical reactions [5-8], is given by

$$\mathbf{F}_A = -\int \rho_1(r) \, Z_A \mathbf{r}_A \, r_A^{-3} \, dr + \sum_{B \neq A} Z_A Z_B \, \mathbf{R}_{AB} \, R_{AB}^{-3} \quad (1.6)$$

thanks to the Hellmann-Feynman theorem [9]. The energy of the system reads

$$E = \int \hat{v}(1) \, \Gamma_1(1';1) \Big|_{1'=1} \, dx_1 + \int \hat{w}(1,2) \, \Gamma_2(1',2';1,2) \, dx_1 \, dx_2 , \quad (1.7)$$

(note that here and in the following the substitution $1' = 1$, $2' = 2$, etc. is omitted for simplicity). Thus, since all the physical quantities are calculated from Γ_2, we may use it as a basic variable of quantum mechanics instead of the wave function Ψ. Further, if we can determine Γ_2 without using Ψ, we have a closed form of quantum mechanics employing Γ_2 instead of Ψ. This method has sometimes been referred to as *'the wave mechanics without wave'*.

Several methods are known for determining the RDM directly without using the wave function. It is straightforward to obtain an explicit expression of the variational formula for the 2-RDM as

$$E_g \leq E[\Gamma_2] \quad \text{and} \quad \delta E[\Gamma_2] = 0, \quad (1.8)$$

where E_g is the ground-state energy. In order to be of physical relevance, the solution Γ_2 must correspond to an N-electron wave function that satisfies the Pauli principle. This condition, referred to as the N-representability condition [10-14], is not yet completely known, hence this variational method is not yet feasible. When one performs variational calculations for Γ_2 using only some known N-representability conditions, one gets the energy that is too low comparing with the exact value [12-14]. There has been, however, progress in our laboratory along this line of the variational approach [15].

Another approach is the variational method for the electron density $\rho_1(r)$ based on the Hohenberg-Kohn theorem [16]. It states that we have the variational theorem for the non-degenerate ground state as a functional of the electron density,

$$E_g \leq E[\rho_1] . \tag{1.9}$$

However, this theorem is only an existence theorem and its explicit form is not known. We have shown that if one knows the external potential v(i) associated to an arbitrary (trial) density $\rho_1(r)$ then the Hohenberg-Kohn theorem can be explicitly written down [17, 18]. This fact was cleverly called by Levy [19] as 'v-representability'. Note that the N-representability condition is known for the electron density $\rho_1(r)$ [10]. Parr and Yang [20] summarized the basic theoretical aspects of this approach. The computational method based on this theorem has been well developed recently as density functional theory (DFT). However, because of the absence of the explicit expression associated with the basic theorem, the DFT approach has a somewhat semi-empirical nature.

In 1976, the author of this chapter presented the equation [21], called density equation (DE), which is equivalent in necessary and sufficient sense with the SE in the domain of the N-representable RDMs. It is written as

$$E \, \Gamma_2(1',2';1,2) = \binom{N}{2} G_2(1',2';1,2) , \tag{1.10}$$

where $G_2(1',2';1,2)$ is the second-order energy density matrix (2-EDM) defined by

$$G_2(1',2';1,2) = \int \Psi^*(1',2',3,...,N) \, \hat{H}(1,2,3,...,N) \, \Psi(1,2,3,...,N) \, dx_3...dx_N . \tag{1.11}$$

Using Eq. (1.3) for the Hamiltonian, the DE is rewritten as

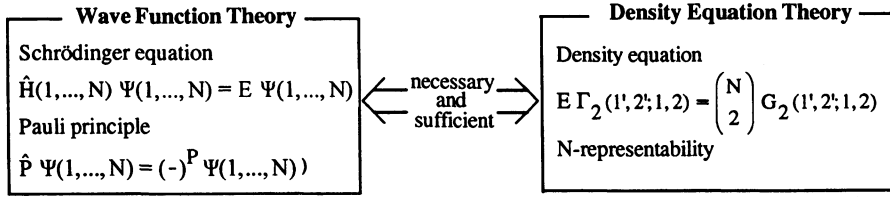| Wave Function Theory		Density Equation Theory
Schrödinger equation $\hat{H}(1,...,N)\ \Psi(1,...,N) = E\ \Psi(1,...,N)$ Pauli principle $\hat{P}\ \Psi(1,...,N) = (-)^{P}\ \Psi(1,...,N))$	$\xleftarrow{}$ necessary $\xrightarrow{}$ and $\xleftarrow{}$ sufficient $\xrightarrow{}$	Density equation $E\,\Gamma_2(1',2';1,2) = \begin{pmatrix} N \\ 2 \end{pmatrix} G_2(1',2';1,2)$ N-representability

Figure 5.1   Wave-function theory and density equation theory.

$$E\,\Gamma_2 = [\hat{v}(1) + \hat{v}(2) + \hat{w}(1,2)]\,\Gamma_2$$
$$+ 3\int [\hat{v}(3) + \hat{w}(1,3) + \hat{w}(2,3)]\,\Gamma_3\ dx_3$$
$$+ 6\int \hat{w}(3,4)\,\Gamma_4\ dx_3\ dx_4, \tag{1.12}$$

which includes not only Γ_2, but also Γ_3 and Γ_4. Solving the DE under the N-representability condition is equivalent to solving the SE under the constraint of the Pauli principle. Fig. 5.1 is an illustration of this equivalence. The author's conjecture is that the EDM including Γ_3 and Γ_4 could be reformulated in terms of only Γ_1 and Γ_2 upon imposing the N-representability condition [22].

In the time-dependent case, the density equation is written as [22]

$$i\hbar\frac{\partial}{\partial t}\Gamma_2(1',2',t';1,2,t) = \begin{pmatrix} N \\ 2 \end{pmatrix} G_2(1',2',t';1,2,t), \tag{1.13}$$

which is equivalent with the time-dependent SE,

$$\hat{H}\,\Psi = i\hbar\frac{\partial}{\partial t}\Psi. \tag{1.14}$$

The author proposes to call the theory that describes the quantum mechanics in terms of only the RDMs *the density matrix theory* (DMT). The DMT naturally includes the DFT, which is based on Eq. (1.9). The method based on the DE, Eq. (1.10) is referred to as *the density equation theory* (DET), and the variational method based on Eq. (1.8) is named *the density matrix variational theory* (DMVT). Thus, the DMT includes the DFT, DET, and DMVT as a family.

Note that Eqs. (1.8) - (1.10) of the DMT are equivalent (in a necessary and sufficient sense) with the SE. This necessary and sufficient equivalence

is very important, since only equations that satisfy it have the same determinative power as the SE. Further, note that these equations claim that the singles (DFT) and the singles and doubles (DMT in a narrow sense) descriptions of quantum mechanics are possible. The origin of the possibility of the singles and doubles description lies in the fact that the Hamiltonian includes only one- and two-particle operators. Recently, the author of this chapter considered the structure of the exact wave function and the possibility of the singles and doubles description of the exact wave function based on this simple structure of the Hamiltonian [23].

The purpose of this chapter is to explain the underlying concept and the recent developments of the DET for a direct determination of the RDM without using the wave function. For a limit of the space and time, most subjects are taken from those developed in the author's laboratory.

2. THE DENSITY EQUATION

The nth-order reduced density matrix (n-RDM), which is assumed to be N-representable, is defined by

$$\Gamma_n(1',...,n';1,...,n)$$

$$= \binom{N}{n} \int \Psi^*(1',...,n',n+1,...N) \, \Psi(1,...,n,n+1,...N) \, dx_{n+1}...dx_N$$

$$\equiv \binom{N}{n} \langle \Psi|\Psi\rangle_n , \tag{2.1}$$

where we introduce a convenient notation of $\langle \ \rangle_n$. The n-RDM satisfies the following recurrence formula

$$\int \Gamma_p(1',...,(p-1)',p;1,...,(p-1),p) \, dx_p$$

$$= \frac{N-p+1}{p} \Gamma_{p-1}(1',...,(p-1)';1,...,(p-1)) . \tag{2.2}$$

Using this Ψ, we define the nth-order energy density matrix (n-EDM) as

$$G_n(1',...,n';1,...,n) = \langle \Psi|\hat{H}|\Psi\rangle_n . \tag{2.3}$$

Then, we define the nth-order density equation (n-DE) by

$$E \; \Gamma_n(1',...,n';1,...,n) = \binom{N}{n} G_n(1',...,n';1,...,n), \qquad (2.4)$$

which satisfies the following theorem:

Theorem: Each of the density equations with $n \geq 2$ is equivalent to the Schrödinger equation in the necessary and sufficient sense [21].

Proof. With the integral notation defined above, the nth-order DE reads

$$\left\langle \Psi \middle| (\hat{H} - E) \middle| \Psi \right\rangle_n = 0. \qquad (2.5)$$

The necessity is trivial: $(\hat{H} - E)\Psi = 0$ implies Eq. (2.5). The sufficiency is proved as follows: We first consider the case of $n = 2$. Then, we have

$$E \; \Gamma_2(1',2';1,2) = \binom{N}{2} G_2(1',2';1,2). \qquad (2.6)$$

By integrating Eq. (2.6), we obtain

$$E \; \Gamma_1(1';1) = N \; G_1(1';1) \qquad (2.7)$$

and

$$E = \left\langle \Psi \middle| \hat{H} \middle| \Psi \right\rangle = \int \hat{v}(1) \; \Gamma_1(1';1) \; dx_1 \; + \; \int \hat{w}(1,2) \; \Gamma_2(1',2';1,2) \; dx_1 \; dx_2. \qquad (2.8)$$

Using Eqs. (2.6) - (2.8), we arrive at

$$\left\langle \Psi \middle| \hat{H}^2 \middle| \Psi \right\rangle = \left\langle \Psi \middle| \hat{H} \middle| \hat{H}\Psi \right\rangle = N \int \hat{v}(1) \; G_1(1';1) \; dx_1$$

$$+ \binom{N}{2} \int \hat{w}(1,2) \; G_2(1',2';1,2) \; dx_1 \; dx_2$$

$$= E \; [\int \hat{v}(1) \; \Gamma_1(1';1) \; dx_1$$

$$+ \int \hat{w}(1,2) \; \Gamma_2(1',2';1,2) \; dx_1 \; dx_2] = E^2. \qquad (2.9)$$

The satisfaction of both Eqs. (2.8) and (2.9) means that Ψ satisfies the SE [24]. When E is degenerate, Ψ is a linear combination of the degenerate states. Thus, the sufficiency is proved for $n = 2$. For the case $n > 2$, the integration of the DE over the last $n - 2$ coordinates yields Eq. (2.6). Thus, the necessary and sufficient theorem is proved. (Q.E.D.)

The n-DE given by Eq. (2.4) is rewritten as

$$E \, \Gamma_n = [\sum_{i}^{n} \hat{v}(i) + \sum_{i>j}^{n} \hat{w}(i,j)] \, \Gamma_n$$

$$+ (n+1) \int [\hat{v}(n+1) + \sum_{i}^{n} \hat{w}(i,n+1)] \, \Gamma_{n+1} \, dx_{n+1}$$

$$+ \frac{1}{2}(n+1)\,(n+2) \int \hat{w}(n+1,n+2) \, \Gamma_{n+2} \, dx_{n+1} \, dx_{n+2}$$

$$(2.10)$$

and

$$\int [\hat{H}_n (1,...,n;n+1,n+2) - E] \, \Gamma_{n+2} \, dx_{n+1} \, dx_{n+2} = 0, \qquad (2.11)$$

where

$$\hat{H}_n (1,...,n;n+1,n+2) = \sum_{i}^{n} \hat{v}(i) + \sum_{i>j}^{n} \hat{w}(i,j)$$

$$+ (N-n) \, [\hat{v}(n+1) + \sum_{i}^{n} \hat{w}(i,n+1)]$$

$$+ \frac{1}{2} \, (N-n) \, (N-n-1) \hat{w}(n+1,n+2). \quad (2.12)$$

For $n = 2$, Eq. (2.10) reduces to Eq. (1.12).

From the theorem, we understand that every DE with $n \geq 2$ is equivalent to the SE for the N-representable RDM. The equivalence shown in Fig. 5.1 holds for each n larger than two. It is guaranteed that the N-representable solution of the DE is identical with the RDM obtained from the solution of the SE by using Eq. (2.1). In the DE, an increase in N does not cause a difficulty in the solution, in contrast to the SE. The DE is applicable to both ground and excited states and to both fermion and boson systems. Among the DEs of different orders, the second-order DE (2-DE) is the simplest and

therefore has much utility. We will discuss in the next section how to solve the 2-DE.

The 1-DE is only a necessary but not a sufficient condition of the SE. It becomes sufficient when the Hamiltonian involves only one-particle terms. The Hartree-Fock (HF) Hamiltonian is one such example.

We note that the DE is not a hierarchy equation. The DE is formally identical with a member of the coupled chain of hierarchy equations derived by Cho [25] and Cohen and Frishberg [26], but they showed only the necessary condition: they derived their equations from the SE but did not prove the converse. Therefore, their equations couple with the higher-order ones up to the SE. On the other hands, each DE with $n \geq 2$ is equivalent to the SE: it does not necessarily couple with the other member of the DEs. Though the n-DE includes not only the n-RDM, but also the (n+1)- and (n+2)-RDMs in the n-EDM, the latter two should be related with the n-RDM by the N-representability condition [22]. Thus, the 2-DE given by Eq. (1.12) is as powerful as all the higher-order DEs. The 1-DE is not as powerful as all the other DEs. Mazziotti [27] has recently presented a second-quantized formulation of the DE.

The theorem given above is both necessary and sufficient: it guarantees that the DE has just the same determinative power as the SE. The only problem that remains unsolved for the singles and doubles description of the quantum mechanics in the DMT is the N-representability.

We note here how important is the necessary and sufficient equivalence. There are several equations that are equivalent in this sense with the SE, including the ordinary variational equation, the Weinstein-McDonald variational equation [24], and some other equations summarized elsewhere [23]. These equations guarantee that their solutions are exact when solved appropriately. The DE is such an equation in the DMT and furthermore it enables the singles and doubles description.

There are many equations that are only necessary conditions of the SE, such as the Hellmann-Feynman theorem [9], the integral Hellmann-Feynman theorem [28], virial theorem [29], etc., but none of them has the determinative power of the SE. For example, one may imagine a calculation of the electron density $\rho_1(r)$ of a molecule in the equilibrium geometry by the Hellmann-Feynman theorem, requiring that the forces acting on the constituent nuclei vanish, but will find it impossible because the Hellmann-Feynman theorem is not a sufficient condition of the SE: the Hellmann-Feynman theorem is not determinative [30]. In a similar sense, we think that the 1-DE is not as useful as the other DEs.

Lastly, we note that calling the DE the contracted Schrödinger equation (CSE) [31] is not adequate for two obvious reasons. First, the CSE is derived only as a necessary condition of the SE, so that it is entirely the same as the

hierarchy equation derived by Cho [25] and Cohen and Frishberg [26]. Second, it was derived much later than the hierarchy equation and the DE, and therefore has no priority at all.

3.   THE HARTREE-FOCK THEORY AS THE ZEROTH-ORDER DET

The n-DE includes not only n-RDM but also (n+1)- and (n+2)-RDMs. The complete N-representability would describe them in terms of the n-RDM [22]. When the system consists of independent particles, namely when the Hamiltonian of the system includes only the one-particle terms, the 1-DE is equivalent (in the necessary and sufficient sense) with the SE. The HF model of the many-fermion system also corresponds to this case. In such a case, the p-RDM of the system is expressed by the 1-RDM as

$$
\Gamma_p^{HF}(1',...,p';1,...,p) = \frac{1}{p!}
\begin{vmatrix}
\Gamma_1^{HF}(1';1) & \Gamma_1^{HF}(1';2) & ... & \Gamma_1^{HF}(1';p) \\
\Gamma_1^{HF}(2';1) & \Gamma_1^{HF}(2';2) & ... & \Gamma_1^{HF}(2';p) \\
... & ... & ... & ... \\
\Gamma_1^{HF}(p';1) & \Gamma_1^{HF}(p';2) & ... & \Gamma_1^{HF}(p';p)
\end{vmatrix},
$$

(3.1)

where the superscript HF stands for the independent-particle model. Thus, in this system, the 2- and 3-RDMs in the 1-DE are certainly expressed in terms of the 1-RDM and Eq. (3.1) guarantees the N-representability of the RDM [2].

When we insert Eq. (3.1) into the DE and assume

$$
\Gamma_1^{HF}(1';1) = \sum_k^N \varphi_k^*(1') \varphi_k(1)
$$

(3.2)

then it is easy to show [21] that the 1-DE turns into

$$
\hat{h}(1) \varphi_k(1) = \sum_l^N \varepsilon_{lk} \varphi_l(1),
$$

(3.3)

where

$$\hat{h}(1) = \hat{v}(1) + \sum_j^N [\hat{J}_j(1) - \hat{K}_j(1)] \qquad (3.4)$$

and

$$\varepsilon_{lk} = \left\langle \varphi_l \left| \hat{h} \right| \varphi_k \right\rangle . \qquad (3.5)$$

Eq. (3.3) is nothing else but the HF equation. Thus, the DE becomes the HF equation for an independent-particle system. The zeroth-order approximation of the DE in the correlation problem is the HF equation, as in the standard correlation theories.

4. THE CORRELATED DENSITY EQUATION

As the HF theory is the zeroth-order approximation of the DET with respect to the electron correlation, it would be instructive to transform the DE in such a way that the electron correlation effects appear explicitly in the solution [21]. For this purpose, we define the correlated density matrix (CDM) as

$$C_p(1',...,p';1,...,p) = \Gamma_p(1',...,p';1,...,p) - \Gamma_p^{HF}(1',...,p';1,...,p) . \qquad (4.1)$$

The CDM includes the correlation correction to all orders. Since Γ_p^{HF} satisfies the same normalization and recurrence formula as the exact RDM Γ_p, we can show that the CDM satisfies the conditions

$$Tr\, C_p = \int C_p(1,...,p;1,...,p)\, dx_1...dx_p = 0 \qquad (4.2)$$

and

$$\int C_p(1',...,(p-1)',p;1,...,(p-1),p)\, dx_p$$

$$= \frac{N-p+1}{p}\, C_{p-1}(1',...,(p-1)';1,...,(p-1)) . \qquad (4.3)$$

The correlated density equation (CDE) that directly determines the CDM is obtained by inserting Eq. (4.1) into the DE and then simplifying the

result with the HF relations given by Eq. (3.3). The 2-DE is transformed into the 2-CDE that reads

$$[\hat{v}(1) + \hat{v}(2) + \hat{w}(1,2) - E] \, C_2 + 3\int \, [\hat{v}(3) + \hat{w}(1,3) + \hat{w}(2,3)] \, C_3 \, dx_3$$

$$+ 6\int \, \hat{w}(3,4) \, C_4 \, dx_3 \, dx_4 + [\hat{w}(1,2) - E^{corr}] \, \Gamma_2^{HF}$$

$$-\int \, \hat{w}(1,3) \, \Gamma_2^{HF}(1',2';1,3) \, \Gamma_1^{HF}(3';2) \, dx_3$$

$$-\int \, \hat{w}(2,3) \, \Gamma_2^{HF}(2',1';2,3) \, \Gamma_1^{HF}(3';1) \, dx_3$$

$$+\int \, \hat{w}(3,4) \, \Gamma_2^{HF}(1',2';3,4) \, \Gamma_2^{HF}(3',4';1,2) \, dx_3 \, dx_4 = 0 \, . \qquad (4.4)$$

This equation includes not only C_2 but also C_3 and C_4, the other terms being known HF quantities. The relations for the 3- and 4-CDM in the EDM with the 1- and 2-CDM are given by the N-representability and/or approximated by physical and mathematical considerations. Since the physical intuition for the CDM may be different from that for the ordinary RDM, the decoupling approximation for the CDM may be more effective than that for the RDM.

The 1-CDE becomes particularly simple as given by [21],

$$[\hat{v}(1) - E] \, C_1 + 2\int \, [\hat{v}(2) + \hat{w}(1,2)] \, C_2 \, dx_2$$

$$+ 3\int \, \hat{w}(2,3) \, C_3 \, dx_2 \, dx_3 \, = E^{corr} \, \Gamma_1^{HF} \, . \qquad (4.5)$$

Some interesting properties of the CDM were summarized in Ref. 21. Among others, from the Hermitian property of the CDM, we can define the natural correlated geminals $\{\eta_i\}$ as

$$C_2(1',2';1,2) = \sum_i \, \mu_i \, \eta_i^*(1',2') \, \eta_i(1,2) \, , \qquad (4.6)$$

where the sum of $\{\mu_i\}$ satisfies

$$\sum_i \, \mu_i = 0 \, . \qquad (4.7)$$

Other N-representability conditions for the CDM are obtained from those for the ordinary RDM [21].

5.   SOLVING THE DE

We consider here the method of solving the 2-DE given by Eq. (1.12). Since we do not yet know the complete N-representability condition, we have to introduce some approximations for expressing the 3- and 4-RDMs in terms of the 1- and 2-RDMs.

There are several methods of approximating the higher-order RDMs in terms of the lower-order ones. The most common one is the independent-particle approximation, which is zeroth-order in the electron-correlation expansion,

$$
\Gamma_3^{HF}(1',2',3';1,2,3) = \frac{1}{3!}
\begin{vmatrix}
\Gamma_1^{HF}(1';1) & \Gamma_1^{HF}(1';2) & \Gamma_1^{HF}(1';3) \\
\Gamma_1^{HF}(2';1) & \Gamma_1^{HF}(2';2) & \Gamma_1^{HF}(2';3) \\
\Gamma_1^{HF}(3';1) & \Gamma_1^{HF}(3';2) & \Gamma_1^{HF}(3';3)
\end{vmatrix}
$$

(5.1)

and

$$
\Gamma_4^{HF}(1',2',3',4';1,2,3,4)
$$
$$
= \frac{1}{4!}
\begin{vmatrix}
\Gamma_1^{HF}(1';1) & \Gamma_1^{HF}(1';2) & \Gamma_1^{HF}(1';3) & \Gamma_1^{HF}(1';4) \\
\Gamma_1^{HF}(2';1) & \Gamma_1^{HF}(2';2) & \Gamma_1^{HF}(2';3) & \Gamma_1^{HF}(2';4) \\
\Gamma_1^{HF}(3';1) & \Gamma_1^{HF}(3';2) & \Gamma_1^{HF}(3';3) & \Gamma_1^{HF}(3';4) \\
\Gamma_1^{HF}(4';1) & \Gamma_1^{HF}(4';2) & \Gamma_1^{HF}(4';3) & \Gamma_1^{HF}(4';4)
\end{vmatrix}.
$$

(5.2)

As shown in section 3, the independent particle model gives the HF equation as the zeroth-order approximation of the DE.

The first-order approximation was given by Valdemoro and her co-workers [32-36]. The 3- and 4-RDMs were approximated as

$$
{}^3D = ({}^1D \times {}^1D \times {}^1D) + ({}^2D \times {}^1D)
$$

(5.3)

and

$$
{}^4D = ({}^1D \times {}^1D \times {}^1D \times {}^1D) + ({}^2D \times {}^1D \times {}^1D) + ({}^3D \times {}^1D),
$$

(5.4)

where ^nD stands for the nth-order spin-free reduced density matrix, which is the spin sum of the n-RDM. These authors derived their equations from the anti-commutation relations of creation and annihilation operators. Eqs. (5.3) and (5.4) are given rather schematically, the detailed explanations being available in the original papers [32-36].

The second-order approximation was derived by the author of this chapter [37-39] with the help of the Green's function method [40]. It reads

$$^3D = \left(\,|\,|\,| + \cdots \right) + \left(|\!\!\rightleftharpoons\!\!|\;| + \cdots \right) + \left(|\!\!\rightleftharpoons\!\!\rightleftharpoons\!\!| + \cdots \right) \tag{5.5}$$

and

$$^4D = \left(\,|\,|\,|\,| + \cdots \right) + \left(|\!\!\rightleftharpoons\!\!|\;|\;| + \cdots \right) + \left(|\!\!\rightleftharpoons\!\!\rightleftharpoons\!\!|\;| + \cdots \right)$$
$$+ \left(|\!\!\rightleftharpoons\!\!|\;\,|\!\!\rightleftharpoons\!\!| + \cdots \right), \tag{5.6}$$

where the first and second terms of Eq. (5.5) are the same as the corresponding terms of Eq. (5.3), and the first three terms of Eq. (5.6) are the same as those of Eq. (5.4). The last term of Eq. (5.6) is referred to as two-pair (2-P) term and is defined as follows: First, we introduce the collision term U as

$$\frac{1}{2}\,[U(1',2';1,2) - U(1',2';2,1)] = \Gamma_2(1',2';1,2) - \frac{1}{2}\begin{vmatrix} \Gamma_1(1';1) & \Gamma_1(1';2) \\ \Gamma_1(2';1) & \Gamma_1(2';2) \end{vmatrix}, \tag{5.7}$$

where the second term in the right-hand side is the 2-RDM in the independent particle approximation given by Eq. (3.1), though the Γ_1 in Eq. (5.7) is not the HF one. Therefore, the collision term U represents the correlation correction to the 2-RDM. The 2-P term in the 4-RDM is given by the appropriate product of the collision term U and therefore it represents the so-called simultaneous collisions. The last term of Eq. (5.5) is referred to as the UV term. A detailed explanation of its origin is given in Refs. 37-39. A different formulation of the UV term was given later by Mazziotti [27, 41].

Since the DE is exact, the accuracy of the 3- and 4-RDMs represented by the 1- and 2-RDMs is the key to the total performance of the DET. Table 5.1 shows the errors in the 3- and 4-RDMs calculated for the Be atom with the above method in comparison with the exact full CI (FCI) values [37]. The errors in the first-order approximation given by Eqs. (5.3) and (5.4) are

Table 5.1 Errors in the first- and second-order approximations to the 3- and 4-RDMs
of the ground state of the Be atom

3-RDM			
Element	*Approximation error*		*FCI value*
$i_1,i_2,i_3;j_1,j_2,j_3$	*First-order*	*Second-order*	
2,3,3;2,3,3	$3.356 \cdot 10^{-4}$	$7.250 \cdot 10^{-7}$	$1.758 \cdot 10^{-4}$
2,2,3;2,2,3	$-3.174 \cdot 10^{-4}$	$-4.751 \cdot 10^{-7}$	$2.029 \cdot 10^{-4}$
2,2,3;1,1,3	$-2.233 \cdot 10^{-4}$	$-2.552 \cdot 10^{-7}$	$2.235 \cdot 10^{-4}$
1,1,3;1,1,3	$-2.015 \cdot 10^{-4}$	$-2.814 \cdot 10^{-7}$	$3.187 \cdot 10^{-4}$
1,3,3;1,3,3	$1.752 \cdot 10^{-4}$	$4.459 \cdot 10^{-7}$	$3.364 \cdot 10^{-4}$
3,3,2;2,3,3	$-1.678 \cdot 10^{-4}$	$-3.625 \cdot 10^{-7}$	$-8.789 \cdot 10^{-5}$
3,2,2;2,2,3	$1.587 \cdot 10^{-4}$	$2.376 \cdot 10^{-7}$	$-1.014 \cdot 10^{-4}$

4-RDM			
Element	*Approximation error*		*FCI value*
$i_1,i_2,i_3i_4;j_1,j_2,j_3,j_4$	*First-order*	*Second-order*	
3,3,2,2;3,3,2,2	$-7.928 \cdot 10^{-5}$	$2.931 \cdot 10^{-7}$	$3.933 \cdot 10^{-5}$
3,3,2,2;3,3,1,1	$-5.581 \cdot 10^{-5}$	$1.169 \cdot 10^{-7}$	$5.591 \cdot 10^{-5}$
3,3,2,2;2,3,2,3	$3.964 \cdot 10^{-5}$	$-1.466 \cdot 10^{-7}$	$-1.967 \cdot 10^{-5}$
3,3,1,1;3,3,1,1	$-3.922 \cdot 10^{-5}$	$1.779 \cdot 10^{-7}$	$7.948 \cdot 10^{-5}$
4,4,2,2;3,3,1,1	$-3.740 \cdot 10^{-5}$	$1.869 \cdot 10^{-8}$	$3.742 \cdot 10^{-5}$
4,4,3,3;2,2,1,1	$-3.652 \cdot 10^{-5}$	$-1.731 \cdot 10^{-7}$	$3.657 \cdot 10^{-5}$
4,3,2,2;3,3,1,1	$2.973 \cdot 10^{-5}$	$-3.329 \cdot 10^{-8}$	$-2.977 \cdot 10^{-5}$
3,3,2,2;1,3,1,3	$2.791 \cdot 10^{-5}$	$-5.844 \cdot 10^{-8}$	$-2.796 \cdot 10^{-5}$
4,4,1,1;3,3,1,1	$-2.628 \cdot 10^{-5}$	$6.203 \cdot 10^{-8}$	$1.631 \cdot 10^{-6}$

almost as large as the values of both the 3- and 4-RDMs, so that the first-order approximation is not adequate, while the errors of the second-order approximation are from two to three orders of magnitude smaller than the values themselves, so that the second-order approximation should work much better. We also have similar results for H_2O and other molecules [42].
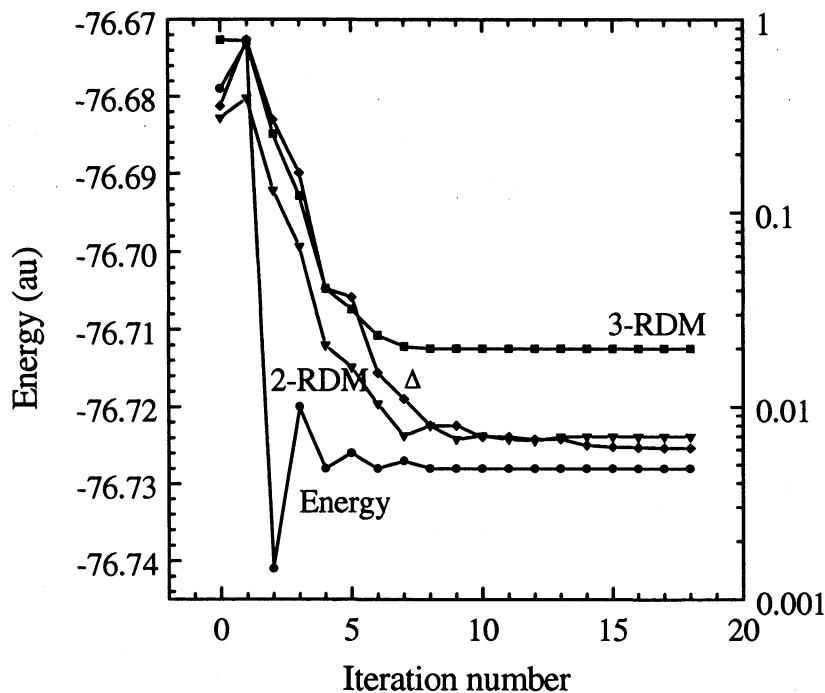
Figure 5.2 Energy and density errors in the iteration process of the H_2O molecule. The density errors are given by the respective square norms of the differences between the DET and FCI densities.

The DE is solved iteratively [37-39]. It is written as

$$\binom{N}{2} G_2[\Gamma_2] - E\,\Gamma_2 = \Delta \tag{5.8}$$

with Δ being zero for the exact Γ_2. The HF Γ_2 is used as the initial guess. We calculate G_2, which is the right-hand side of Eq. (1.12), using the second-order approximation for Γ_3 and Γ_4 given by Eqs. (5.5) and (5.6). We then calculate Δ from Eq. (5.8) and from it we estimate the updated Γ_2. The Newton-Raphson method was found useful in this procedure. We normalize the new Γ_2, check its N-representability, and calculate a new energy E from it. We repeat the iterations until convergence. More details of our method are given in Refs. 37-39.

Fig. 5.2 shows the behavior of the energy, the 2-RDM, and the related quantities during the iteration process for the H_2O molecule. The energy converges nicely within 6 iterations and other quantities within 10 iterations. The converged 3-RDM differs somewhat from its FCI counterpart because our Eq. (5.5) for Γ_3 is only approximate.

Table 5.2 Energies and properties calculated by the DET and the wave function theory

Molecule[a]	DET	HF	SDCI	FCI[b]
	Energy in au (percentage error in correlation energy) Dipole or quadrupole moment in au[c]			
H_2O (5×9, 10)	-76.14827 (6.48) 0.9801	-76.00984 (100) 1.0142	-76.15001 (5.30) 0.9826	-76.15787 (0.0) 0.9762
NH_3 (4×10, 8)	-56.29888 (4.24) 0.9098	-56.17599 (100) 0.9226	-56.29717 (5.58) 0.9133	-56.30433 (0.0) 0.9081
CH_4 (4×12, 8)	-40.29582 (3.73) 0.0	-40.18546 (100) 0.0	-40.29405 (5.27) 0.0	-40.30009 (0.0) 0.0
HF (4×12, 8)	-100.21876 (2.85) 0.7920	-100.02179 (100) 0.8215	-100.21622 (4.10) 0.7931	-100.22453 (0.0) 0.7919
N_2 (5×11, 10)	-109.07909 (12.27) 2.046	-108.87826 (100) 1.808	-109.08219 (10.92) 1.993	-109.10719 (0.0) 2.054
CO (5×11, 10)	-112.87293 (12.99) 0.0344	-112.68505 (100) -0.1652	-112.87382 (12.58) 0.0586	-112.90098 (0.0) 0.0445
C_2H_2 (5×15, 10)	-76.98006 (6.37) 4.642	-76.79907 (100) 5.315	-76.97559 (8.65) 4.817	-76.99230 (0.0) 4.762
CH_3OH (7×5, 14)	-114.71144 (5.24) 0.6024	-114.58982 (100) 0.6548	-114.71082 (5.72) 0.6058	-114.71816 (0.0) 0.5991
CH_3NH_2 (7×6, 14)	-95.06781 (3.76) 0.5634	-94.93849 (100) 0.5754	-95.06505 (5.81) 0.5633	-95.07286 (0.0) 0.5619
C_2H_6 (stag.) (7×7, 14)	-79.20924 (0.24) 0.4279	-79.06233 (100) 0.4589	-79.20448 (3.47) 0.4307	-79.20959 (0.0) 0.4284
C_2H_6 (ecl.) (7×7, 14)	-79.20405 (0.20) 0.4843	-79.05686 (100) 0.5159	-79.19925 (3.46) 0.4876	-79.20435 (0.0) 0.4851

[a] The active space and the number of electrons in it are given in parentheses.
[b] MP4 energies for N_2, CO, C_2H_2, and C_2H_6; CISDTQ moments for N_2, CO, and C_2H_6; and the CISDT quadrupole moment for C_2H_2.
[c] Quadrupole moment is given in case of zero dipole moment.

Our final results [38] are summarized in Table 5.2 for the following molecules: H_2O, NH_3, CH_4, HF, N_2, CO, C_2H_2, CH_3OH, CH_3NH_2, and C_2H_6 in the staggered and eclipsed conformations. These were the first molecules for which the DET was successfully applied; the 2-RDMs of these molecules were calculated for the first time directly without any reference to the wave functions. The basis set was of the double-zeta quality for the first seven molecules and STO-6G for the last four ones [38]. The energies (in au), the percentage errors in correlation energies (in parentheses), and the dipole or quadruple moments (in au) are listed. The active space is given in each case by the number of occupied active MOs × the number of unoccupied active MOs and the number of active electrons is listed. The DET results are compared with the results of the HF approximations, the single and double CI (SDCI), and the FCI.

First, let us examine the energy. The DET results are better than the SDCI ones for eight molecules and worse for three molecules. Generally, the larger the molecules the better are the DET results. Next, let us consider the electronic properties. The DET results are better than the SDCI ones for eight molecules and worse for two molecules. As the DET directly determines the RDMs, the accuracy of the related properties should be high. For the energy, the result of the variational method like SDCI is good to the square of the errors involved, while the DET does not have such a property. We may conclude that the DET results shown in Table 5.2 are satisfactory, considering that they are the very first results obtained with DET.

Next, we examine the N-representability of the calculated Γ_2. Some necessary conditions of the N-representability are the positive semi-definite properties of the RDM (P-condition), the hole RDM (Q-condition), and the following g-matrix (G-condition) [12]

$$g(1',2';1,2) = \Gamma_2(1,2';1',2) + \delta(1-1')\Gamma_1(2';2) - \Gamma_1(1';2')\,\Gamma_1(1;2). \quad (5.9)$$

For the 1-RDM, the N-representability condition is that its eigenvalues must fall between zero and two [10].

Table 5.3 lists the minimum eigenvalues of the second-order RDMs, the hole RDMs (HRDMs), and the g-matrices. It also lists the range of the eigenvalues of the 1-RDM. We see that our 2-RDMs do not satisfy the N-representability condition: some eigenvalues of the 2-RDMs, 2-HRDMs, and g-matrices are negative, though they are small. However, the computed 1-RDMs are fully N-representable.

From our experience, we know that when the 2-RDM is far from being N-representable, the convergence of our iterative procedure is poor or even non-existent. Avoiding such a situation by some theoretical method is the topic of the next section.

Table 5.3 The minimum eigenvalues of the 2-RDM, 2-HRDM, and g-matrix, and the range
of the eigenvalues of the 1-RDM calculated with the DET

Molecule[a]	*2-RDM* P	*2-HRDM* Q	*g-matrix* G	*1-RDM*
H_2O (5×9, 10)	$-3.34 \cdot 10^{-4}$	$-1.85 \cdot 10^{-4}$	$-3.28 \cdot 10^{-4}$	$1.94 \cdot 10^{-4}$ ... 1.9998
NH_3 (4×10, 8)	$-4.59 \cdot 10^{-4}$	$-1.46 \cdot 10^{-4}$	$-2.70 \cdot 10^{-4}$	$3.00 \cdot 10^{-4}$ ... 1.9838
CH_4 (4×12, 8)	$-5.71 \cdot 10^{-4}$	$-1.59 \cdot 10^{-4}$	$-3.22 \cdot 10^{-4}$	$2.35 \cdot 10^{-4}$ ... 1.9815
CH_3OH (7×5, 14)	$-5.39 \cdot 10^{-4}$	$-4.35 \cdot 10^{-4}$	$-5.39 \cdot 10^{-4}$	$1.78 \cdot 10^{-2}$ ... 1.9974
N_2 (5×11, 10)	$-1.02 \cdot 10^{-3}$	$-5.31 \cdot 10^{-4}$	$-3.70 \cdot 10^{-3}$	$4.30 \cdot 10^{-4}$ ... 1.9866
CO (5×11, 10)	$-7.83 \cdot 10^{-4}$	$-3.37 \cdot 10^{-4}$	$-6.40 \cdot 10^{-3}$	$5.51 \cdot 10^{-4}$ ... 1.9884
C_2H_2 (5×15, 10)	$-1.52 \cdot 10^{-3}$	$-5.94 \cdot 10^{-4}$	$-3.10 \cdot 10^{-3}$	$3.40 \cdot 10^{-5}$ ... 1.9796

[a] The active space and the number of electrons it contains are given in parentheses.

6.   A GEMINAL EQUATION DERIVED FROM THE DE

In the previous section of this chapter, we have found that the 2-RDMs calculated by the above method do not satisfy the N-representability condition. In particular, our Γ_2 is not positive semi-definite. We describe here a method to constrain our RDM to be positive semi-definite, which naturally leads to a geminal equation. This is somewhat similar to the fact that the HF equation is derived from the DE by imposing the independent particle approximation to the RDMs involved in the DE [21].

In quantum chemistry, the concept of a geminal is very old. Many contributions to the development of this concept have been published [43-49]. However, in modern computational chemistry, it is not much utilized mainly because the orbital concepts are much simpler and can be extended to electron correlation problems by using the CI and the coupled-cluster theories

more efficiently than the conventional geminal approaches. For the history and the recent development in the theory of geminals see Ref. 49.

We expand Γ_2 with a complete set of two-particle functions $\{\phi_i(1,2)\}$ as

$$\Gamma_2(1',2';1,2) = \sum_{ij} d_{ij} \, \phi_i^*(1',2') \, \phi_j(1,2) = \phi^+(1',2') \, \mathbf{d} \, \phi(1,2), \qquad (6.1)$$

where $\phi(1,2)$ is a column vector whose elements are $\{\phi_i(1,2)\}$. We constrain the matrix $\mathbf{d}$ with

$$\mathbf{d} = \mathbf{c}^+\mathbf{c}, \qquad (6.2)$$

hence $\mathbf{d}$ is positive semi-definite and Hermitian [50]. We define

$$\eta(1,2) = \mathbf{c} \, \phi(1,2), \qquad (6.3)$$

obtaining

$$\Gamma_2(1',2';1,2) = \sum_i \eta_i^*(1',2') \, \eta_i(1,2), \qquad (6.4)$$

where $\{\eta_i(1,2)\}$ satisfy the equation

$$\int \eta_i^*(1,2) \, \eta_j(1,2) \, dx_1 \, dx_2 = \delta_{ij} \, \lambda_i^2, \qquad (6.5)$$

which shows that $\{\eta_i(1,2)\}$ are unnormalized geminals. The normalized geminals are obtained from

$$\varphi_i(1,2) = \lambda_i^{-1} \, \eta_i(1,2), \qquad (6.6)$$

yielding

$$\Gamma_2(1',2';1,2) = \sum_i \lambda_i^2 \, \varphi_i^*(1',2') \, \varphi_i(1,2). \qquad (6.7)$$

From the normalization condition,

$$\sum_i \lambda_i = \binom{N}{2}. \tag{6.8}$$

When we solve the DE taking $\{\eta_i(1,2)\}$ or $\{\varphi_i(1,2)\}$ as basic variables instead of Γ_2 itself, the DE produces geminal equation. Since Eq. (6.2) guarantees Γ_2 to be always positive semi-definite and Hermitian, improved convergence and accuracy are expected.

   To utilize the above idea in the DE given by Eq. (1.12), Γ_3 and Γ_4 must be expressed as products of Γ_2 and Γ_1. A simple approach to doing so is to utilize Eqs. (5.1) and (5.2) as follows: For Γ_3, we expand Eq. (5.1) by the third row, replace the 2×2 cofactor by Γ_2, and obtain

$$\Gamma_3(1',2',3';1,2,3) \simeq \frac{1}{3} [\Gamma_2(1',2';1,2)\,\Gamma_1(3';3) - \Gamma_2(1',2';1,3)\,\Gamma_1(3';2)$$

$$+\Gamma_2(1',2';2,3)\,\Gamma_1(3';1)], \tag{6.9}$$

where Γ_1 is derived from Γ_2 through Eq. (1.5). For Γ_4, we similarly expand Eq. (5.2) by the first two rows as

$$\Gamma_4(1',2',3',4';1,2,3,4)$$

$$\simeq \frac{1}{6} [\,\Gamma_2(1',2';1,2)\,\Gamma_2(3',4';3,4) + \Gamma_2(1',2';3,4)\,\Gamma_2(3',4';1,2)$$

$$- \Gamma_2(1',2';1,3)\,\Gamma_2(3',4';2,4) - \Gamma_2(1',2';2,4)\,\Gamma_2(3',4';1,3)$$

$$+ \Gamma_2(1',2';1,4)\,\Gamma_2(3',4';2,3) + \Gamma_2(1',2';2,3)\,\Gamma_2(3',4';1,4)\,] . \tag{6.10}$$

The 4-RDM is also approximated by products of Γ_1 and Γ_3 as

$$\Gamma_4(1',2',3',4';1,2,3,4)$$

$$\simeq \frac{1}{4} [\,\Gamma_3(1',2',3';1,2,3)\,\Gamma_1(4';4) - \Gamma_3(1',2',3';1,2,4)\,\Gamma_1(4';3)$$

$$+\Gamma_3(1',2',3';1,3,4)\,\Gamma_1(4';2) - \Gamma_3(1',2,'3';2,3,4)\,\Gamma_1(4';1)], \tag{6.11}$$

where we have expanded by the last row. Another possibility is to approximate Γ_4 by an appropriate average of Eqs. (6.10) and (6.11). Note that the above formulae do not deal with all the three or four electrons equivalently, but for example in Eq. (6.10), the electrons (1,2) are treated as the variables of Γ_2, while the electrons (3,4) are dealt with as representing all the remain-

ing N - 2 electrons that are finally integrated out in the DE, so that the required symmetry is satisfied within the electron pairs (1,2) and (3,4) but not between them. As seen from the above formulation, it is also possible to derive an approximate formula that satisfies the symmetries for all the electrons involved. Actually, many different approximations are possible along those lines, so searching for the best one is an interesting subject.

Next, we transform the DE using the approximations given by Eqs. (6.9) and (6.10). Putting these equations into the DE given by Eq. (1.12), we obtain

$$[\hat{v}(1) + \hat{v}(2) + \hat{w}(1,2)] \, \Gamma_2(1',2';1,2)$$

$$- \int \hat{v}(3) \, [\Gamma_2(1',2';1,3) \, \Gamma_1(3';2) + \Gamma_2(1',2';3,2) \, \Gamma_1(3';1)] \, dx_3$$

$$+ \int [\hat{w}(1,3) + \hat{w}(2,3)] \, [\Gamma_2(1',2';1,2) \, \Gamma_1(3';3) - \Gamma_2(1',2';1,3) \, \Gamma_1(3';2)$$

$$- \Gamma_2(1',2';3,2) \, \Gamma_1(3';1)] \, dx_3$$

$$+ \int \hat{w}(3,4) \, \Gamma_2(1',2';3,4) \, \Gamma_2(3',4';1,2) \, dx_3 \, dx_4$$

$$+ 2 \int \hat{w}(3,4) \, [\Gamma_2(1',2';1,4) \, \Gamma_2(3',4';2,3)$$

$$+ \Gamma_2(1',2';2,3) \, \Gamma_2(3',4';1,4)] \, dx_3 \, dx_4 = 0 \, . \qquad (6.12)$$

We note here that this equation does not include the term containing the energy E like the term on the left-hand side of Eq. (1.12). This term is actually cancelled by the terms arising from the first terms of Eqs. (6.9) and (6.10). Other approximations to Γ_3 and Γ_4 do not lead to such a cancellation. The new DE given by Eq. (6.12) may be solved by the method similar to the one described in the preceding section of this chapter.

In this section, the purpose is to constrain our Γ_2 to be positive semidefinite. Inserting the geminal expression for Γ_2 given by Eq. (6.4) and performing some manipulations, we obtain the geminal equation as

$$[\hat{v}(1) + \hat{v}(2) + \hat{J}(1) + \hat{J}(2) + \hat{w}(1,2)] \, i(1,2)$$

$$- \int [\hat{v}(3) + \hat{w}(1,3) + \hat{w}(2,3)] \, [i(1,3) \, \Gamma_1(3';2) - i(2,3) \, \Gamma_1(3';1)] \, dx_3$$

$$+ \sum_k k(1,2) \, \langle k(3,4) | \hat{w}(3,4) \, | i(3,4) \rangle$$

$$+ 2 \sum_k \int i(1,4) \, k(2,3) + i(2,3) \, k(1,4)] \, \hat{w}(3,4) \, k(3',4') \, dx_3 \, dx_4 = 0 \, , (6.13)$$

where i(1,2) is a shorthand for $\eta_i(1,2)$ and $\hat{J}(1)$ is the Coulomb repulsion operator defined by

$$\hat{J}(1) = \int \hat{w}(1,2)\, \Gamma_1(2';2)\, dx_2 \ .$$

(6.14)

The energy of the system is calculated from

$$E = \int \hat{v}(1)\, \Gamma_1(1';1)\, dx_1 + \sum_i \left\langle i(1,2) \middle|\, \hat{w}(1,2)\, \middle| i(1,2) \right\rangle.$$

(6.15)

In actual calculations, it is convenient to expand the geminal function i(1,2) with the reference orbital set {a(1)} as

$$i(1,2) = \sum_{ab} C^i_{ab}\, a(1)\, b(2)\ ,$$

(6.16)

which turns Eq. (6.13) into

$$\sum_{ab} C^i_{ab}\, [\langle g|\hat{v}+\hat{J}|a\rangle\, \delta_{bh} + \langle h|\hat{v}+\hat{J}|b\rangle\, \delta_{ag} + \langle gh|\hat{w}|ab\rangle]$$

$$- \sum_{ab} C^i_{ab} \sum_{cd} Q_{cd}\, [\langle c|\hat{v}|b\rangle\, (\delta_{ga}\delta_{hd} - \delta_{gd}\delta_{ha}) + \langle gc|\hat{w}|ab\rangle\, \delta_{hd}$$

$$+ \langle hc|\hat{w}|db\rangle\, \delta_{ga} - \langle gc|\hat{w}|db\rangle\, \delta_{ha} - \langle hc|\hat{w}|ab\rangle\, \delta_{gd}]$$

$$+ \sum_{ab} C^i_{ab} \sum_{cd} \sum_{ef} P_{ef,cd}\, [\langle ef|\hat{w}|ab\rangle\, \delta_{gc}\, \delta_{hd} + 2\langle ef|\hat{w}|db\rangle\, \delta_{ga}\, \delta_{hc}$$

$$+ 2\langle ef|\hat{w}|bd\rangle\, \delta_{gc}\, \delta_{ha}] = 0 \ ,$$

(6.17)

where

$$P_{ab,cd} = \sum_i C^{i*}_{ab}\, C^i_{cd}\ ,$$

(6.18)

$$Q_{ac} = \frac{2}{N-1} \sum_b P_{ab,cb}\ ,$$

(6.19)

and

$$\langle ab| \hat{w} | cd \rangle = \langle a(1)\ b(2)| \hat{w}(1,2)| c(1)\ d(2) \rangle . \tag{6.20}$$

The meaning of the density matrices **P** and **Q** in the reference space follows from

$$\Gamma_2 (1',2';1,2) = \sum_i i^*(1',2')\ i(1,2) = \sum_{ab} \sum_{cd} P_{ab,cd}\ a(1')\ b(2')\ c(1)\ d(2) \tag{6.21}$$

and

$$\Gamma_1 (1';1) = \frac{2}{N-1} \int \Gamma(1',2;1,2)\ dx_2 = \sum_{ab} Q_{ab}\ a^*(1')\ b(1) . \tag{6.22}$$

The energy of the system is given by

$$E = \sum_{ab} Q_{ab} \langle a| \hat{v} | b \rangle + \sum_{ab} \sum_{cd} P_{ab,cd} \langle ab| \hat{w} | cd \rangle . \tag{6.23}$$

Thus, the geminal equation has been derived from the DE. Since this formulation guarantees the positive semi-definiteness of Γ_2, improved convergence and accuracy of the solution are expected. We are currently examining the solution of the above equations, in addition to considering what approximations to Γ_3 and Γ_4 in the EDM are the most appropriate and what accuracy of the calculated results should be expected.

7.   APPLICATION OF DET TO THE CALCULATION OF POTENTIAL ENERGY SURFACES

Structures, reactions, and properties are the three big pillars that support chemical sciences. The potential energy surface (PES) of a system is directly related to these subjects, hence our first concern after the initial success with solving the DE without using the wave function was to examine the possibility of applying DET to calculations of PESs of molecules. We show here the results [51], obtained with the method described in section 3 of this chapter.

When we elongated bonds from their equilibrium lengths, we observed that the convergence of the DE became poorer for some molecules. This was expected since our method is based on the Green's function method and cor-
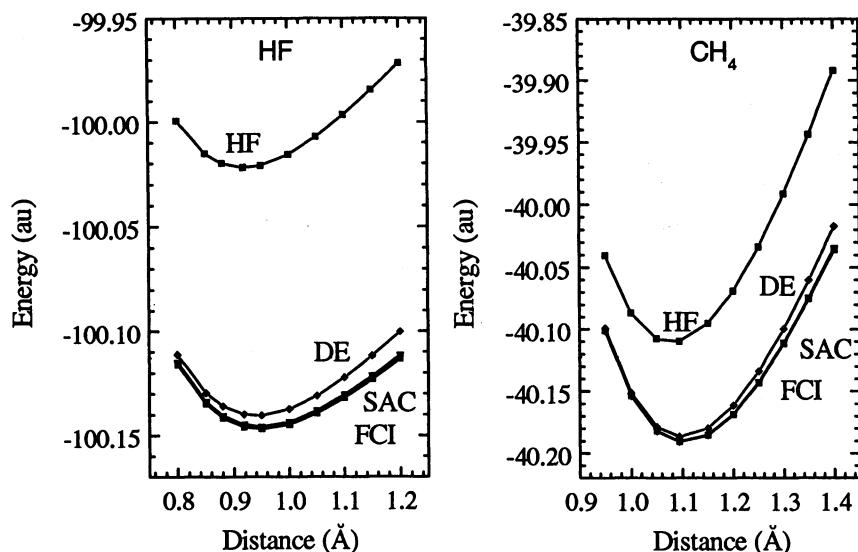
Figure 5.3 Potential energy curves of the HF and CH_4 molecules calculated with the HF, DE, SAC, and FCI methods.

rect to second order with respect to electron correlation. Upon elongation of the C-H bond in CH_4, for example, the well-known quasi-degenerate, multi-reference problem arises and the HF wave function is not a good zeroth-order approximation. When we analyzed the non-convergence problem in our DET, we found that it originated from the breakdown of the N-representability of the inner-core MO; the occupation number of the inner-core MO happened to exceed two. Since the inner-core MO is very stable, electrons tend to occupy it too much when one does not impose the complete set of N-representability conditions.

We have avoided this difficulty by employing the frozen-core approximation. Though this is not a fully satisfactory solution, it certainly works well. Fig. 5.3 shows the potential energy curves of HF and CH_4 molecules calculated with the DET. It also shows the FCI results, which are the exact ones within the basis set used, the HF results, and the data obtained with the SAC (Symmetry Adapted Cluster) method [52-55]. For closed-shell molecules, the SAC results are identical with the coupled cluster (CC) ones. The calculation level was singles and doubles (SD). We see from inspection of Fig. 5.3 that the DE2 (which means the density equation method correct to second order) results are close to the FCI ones for a wide range of internuclear distances. At present, the SAC results are much better than their DET counterparts in both accuracy and efficiency.

Table 5.4 The equilibrium bond lengths and the totally symmetric harmonic frequencies
calculated with different methods

Molecule	Method	R_e (Å)	ω_e (cm^{-1})
HF	HF	0.9195	4025
	DET	0.9416	3778
	SAC	0.9487	3639
	FCI	0.9495	3619
CH$_4$	HF	1.0783	3535
	DET	1.0998	3306
	SAC	1.1035	3245
	FCI	1.1038	3240
BH$_3$	HF	1.1539	3114
	DET	1.1743	2929
	SAC	1.1774	2879
	FCI	1.1778	2884

Table 5.4 lists the equilibrium bond lengths and the totally symmetric
harmonic vibrational frequencies of the HF, CH$_4$, and BH$_3$ molecules. The
DET results are close to those obtained with the SAC and FCI methods. The
bond lengths are correct to within 0.01 Å and the frequencies to within 200
cm^{-1}. Fig. 5.4 shows the dipole moment vs. the bond distance for the HF
molecule. The DET reproduces the FCI result quite well, whereas the HF
result is very different. More details about the results of the DET for the
properties related to the PES are given in Ref. 51.

8.   DET FOR OPEN-SHELL SYSTEMS

The DET described in section 3 of this chapter was applied to open-
shell systems [39]. The calculations for closed-shell systems reviewed in
sections 3 and 7 were carried out using the spin-free RDMs in which the spin
variables were summed up, while the calculations for open-shell systems
were done using the spin-dependent reduced density matrices (SRDMs).
Actually, the formulations and the basic equations given in section 3 were
for general open-shell systems, since the spin-sum was not done there. For
Γ_2, the SRDM has 16 times more variables than the RDM, so that the open-
shell systems are computationally more demanding than the closed-shell
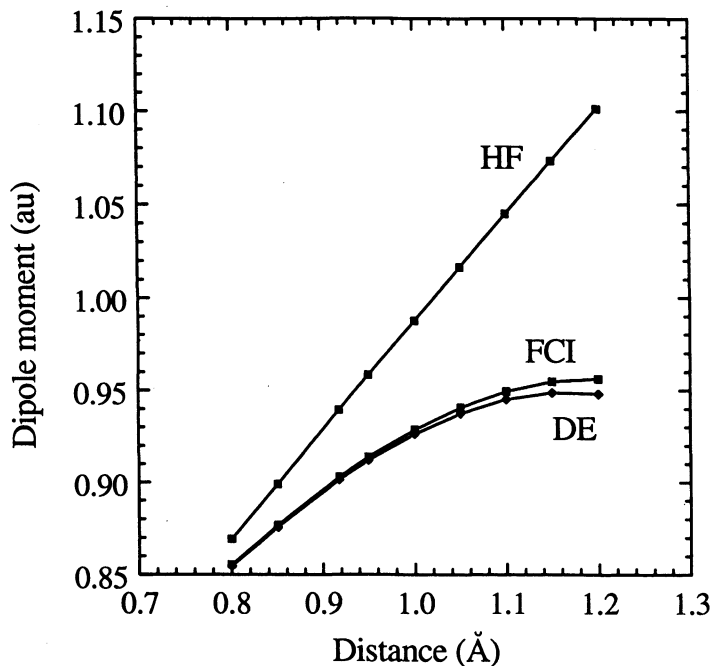ones.

Figure 5.4 The dependence of the dipole moment of the HF molecule on the H-F bond distance calculated with the HF, DE, and FCI methods.

The computational algorithm was the same as in the closed-shell case, but the convergence was less satisfactory. So far, we could calculate only atoms. The calculations were done using only s-type basis sets, so that the doublet states of the five-electron atoms are not the ground ^2P states but actually the excited ^2S states and the triplet states of the four-electron atoms are also not the ^3P states but the ^3S states. Computationally, such S states are easier to calculate than the P states. For more details, see Ref. 39.

Table 5.5 shows the results for the open-shell five-electron doublet and four-electron triplet atoms. The DET data are compared with the results of the HF and FCI methods. The correlation energy errors of the DET results are all smaller than one percent. Though these results are more accurate than those for the closed-shell molecules given in Table 5.2, one should note that the open-shell atoms calculated here are all very small. Table 5.6 lists transition energies, electron affinities, and ionization potentials calculated with the DET. Since the states involved are not the normal ground and excited states,

Table 5.5 Results for the open-shell doublet and triplet states

Atom (State)	DET	HF	FCI
	Energy in au *(percentage error in correlation energy)* *Error norm of the 2-RDM*		
Be (^{2}S)	-13.24020 (-0.1489) $2.20 \cdot 10^{-3}$	-13.21284 (100) $2.79 \cdot 10^{-1}$	-13.24016 (0.0) 0.0
B (^{2}S)	-24.11436 (-0.300) $6.03 \cdot 10^{-3}$	-24.09747 (100) $2.28 \cdot 10^{-1}$	-24.11431 (0.0) 0.0
C$^+$ (^{2}S)	-36.55658 (-0.19032) $3.77 \cdot 10^{-3}$	-36.54203 (100) $1.24 \cdot 10^{-1}$	-36.55655 (0.0) 0.0
N^{2+} (^{2}S)	-51.61476 (-0.1339) $2.47 \cdot 10^{-4}$	-51.60237 (100) $1.73 \cdot 10^{-2}$	-51.61474 (0.0) 0.0
Be (^{3}S)	-13.31466 (-0.1373) $1.43 \cdot 10^{-3}$	-13.30361 (100) $2.67 \cdot 10^{-2}$	-13.31464 (0.0) 0.0
B$^+$ (^{3}S)	-23.60534 (-0.1630) $5.21 \cdot 10^{-3}$	-23.59233 (100) $2.66 \cdot 10^{-2}$	-23.60532 (0.0) 0.0
C^{2+} (^{3}S)	-35.30435 (-0.2936) $6.10 \cdot 10^{-3}$	-30.29153 (100) $2.14 \cdot 10^{-2}$	-35.30431 (0.0) 0.0
N^{3+} (^{3}S)	-49.36284 (-0.1940) $4.54 \cdot 10^{-3}$	-49.34853 (100) $2.32 \cdot 10^{-2}$	-49.36281 (0.0) 0.0

the values themselves may look strange, but in comparison with the FCI results, the DET data are quite close. Table 5.7 lists the electron and spin densities at nuclei of open-shell doublet and triplet atoms. The latter densities are very important quantities measured in ESR experiments. The agreement between the DET and FCI results is good. Since the spin densities calculated

Table 5.6 Transition energies, electron affinities, and ionization potentials (au).

Atom	Process	DET	HF	FCI
B	$^2S + e \rightarrow \, ^1S$	0.44528	0.44083	0.44526
	$^2S - e \rightarrow \, ^1S$	-0.13472	-0.13687	-0.13500
B^+	$^1S \rightarrow \, ^3S$	0.64374	0.64202	0.64399
C^{2+}	$^1S \rightarrow \, ^3S$	1.11340	1.11230	1.11345
	$^1S + e \rightarrow \, ^2S$	-0.13884	-0.13824	-0.13879
N^{3+}	$^1S \rightarrow \, ^3S$	1.72478	1.72571	1.72479
	$^1S + e \rightarrow \, ^2S$	-0.52714	-0.52815	-0.52714

Table 5.7 Electron and spin densities (ρ and ρ_s) at nuclei (au)

Atom (State)	Property	DET	HF	FCI
$Be^- \, (^2S)$	ρ	33.568		33.568
	ρ_s	2.249		2.253
$B \, (^2S)$	ρ	70.058	69.998	70.058
	ρ_s	1.902	1.594	1.896
$C^+ \, (^2S)$	ρ	125.313	125.238	125.313
	ρ_s	2.753	2.380	2.746
$N^{2+} \, (^2S)$	ρ	203.820	203.732	203.820
	ρ_s	3.843	3.396	3.836
$Be \, (^3S)$	ρ	32.530	32.401	32.530
	ρ_s	3.608	2.785	3.603
$B^+ \, (^3S)$	ρ	68.741	68.680	68.742
	ρ_s	3.691	3.215	3.708
$C^{2+} \, (^3S)$	ρ	122.143	122.064	122.142
	ρ_s	6.860	6.103	6.836
$N^{3+} \, (^3S)$	ρ	197.798	197.705	197.798
	ρ_s	11.316	10.273	11.287

within the restricted HF approximation do not include the spin-polarization effects [56, 57], they are always smaller than the DET and FCI values.

9. CONCLUSION AND FUTURE PROSPECTS

The dream of describing quantum mechanics with only the density matrix, namely, the construction of the DMT, has long been held by many scientists. This chapter describes progress achieved in the author's laboratory at Kyoto University towards realization of this dream. The first opportunity for the author to enter into the DMT was the presentation in 1973 of the Hellmann-Feynman force concept for predicting molecular geometries and chemical reactions [6-8]. It has been already 24 years since the author made the first contribution to the DET by presenting the DE [21]. At that moment, the author was rather strict and tried to solve the DE without any approximations, since the DE seemed to imply that a singles and doubles description of quantum mechanics is possible. The N-representability was a big obstacle. Further, compared with the present days, the computational situation was very, very, poor in author's laboratory.

Now the situation is quite different. How helpful is the use of powerful computers in making a progress! A clue in the application of the DE was given by Valdemoro [32-36] by her proposal to solve the DE, even if approximately. We reformulated her approach with the Green's function method and, realizing the importance of the second-order terms, obtained the results described in the sections 3, 7, and 8 of this chapter. Later, Mazziotti [41, 58, 59], Yasuda [60], and Valdemoro [61, 62] proposed some refined methods that show some promise. The geminal equation approach described in the section 4 is also expected to work. Certainly, the cumulant expansion method [63] is useful in the formalism [41, 58, 64, 65]. The density matrix functional theory (DMFT) [20, 66, 67] that is based on $\Gamma_1(1';1)$ instead of $\rho_1(r)$ is also very interesting. This approach clearly belongs to the DMT and may be classified as a member of the DFT because of the similarity in basic approach. Anyway, it is clear that much progress should be done for truly realizing the dream of describing quantum mechanics (chemistry) by the RDM alone.

It may be safe to conclude this chapter by saying that the DET has been applied to a bit of real chemistry: Γ_2 and E of atoms and molecules were directly calculated, to good accuracy, by the DET without any use of the wave function. The 3- and 4-RDMs in the EDM of the DE were approximated by products of Γ_1 and Γ_2. The calculated Γ_2 were almost N-representable and Γ_1 were N-representable. The DET was also used to calculate the potential

energy surfaces of molecules, yielding equilibrium geometries and vibrational force constants, and further applied to open-shell atoms.

The author is quite optimistic about the future of the DET. First, the N-representability problem should be studied not only mathematically but also from a physical standpoint. In the DET, the key is a good representation of Γ_3 and Γ_4 in the EDM in terms of Γ_1 and Γ_2, on which both the accuracy and the convergence of the DE strongly depend. This representation is closely related to the N-representability, so that we have to try to get good ideas based on both physical and mathematical intuitions. The DE is just equivalent to the SE, so that the DET would be suitable for obtaining very accurate solutions for quantum-mechanical problems. Since the RDM is a local property, constructing an N-order theory should be easy in comparison with the wave function approach. Anyway, a small window has been opened and a lot of exciting dreams must exist in future!

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REFERENCES

1. K. Husimi, *Proc. Phys. Math. Soc. Jap.* **22**, 264 (1940).
2. P. -O. Löwdin, *Phys. Rev.* **99**, 1474, 1490 (1955).
3. R. McWeeny, *Rev. Mod. Phys.* **32**, 335 (1960).
4. E. R. Davidson, *Reduced Density Matrices in Quantum Chemistry*, Academic, New York (1976).
5. B. M. Deb (ed.), *The Force Concept in Chemistry*, Van Nostrand Reinhold, New York (1978).
6. H. Nakatsuji, *J. Am.Chem. Soc.* **95**, 345, 354, 2084 (1973); **96**, 24, 30 (1974).
7. H. Nakatsuji, *Kagaku (Chemistry)* **28**, 17, 108 (1973).
8. H. Nakatsuji and T. Koga, in *The Force Concept in Chemistry*, B. M. Deb (ed.), Van Nostrand Reinhold, New York (1981), p. 137.
9. H. Hellmann, *Einführung in die Quantenchemie*, Franz Deuticke, Leipzig (1987), p. 285; R. P. Feynman, *Phys. Rev.* **56**, 340 (1939).
10. A. J. Coleman, R*ev. Mod. Phys.* **35**, 668 (1963).
11. R. M. Erdahl, *J. Math. Phys.* **13**, 1608 (1972).
12. C. Garrod and J. K. Percus, *J. Math. Phys.* **6**, 763 (1964).
13. C. Garrod and M. Rosina, *J. Math. Phys.* **10**, 1855 (1969).
14. L. J. Kijewski, *Phys. Rev.* A **6**, 31 (1972); A **9**, 2263 (1974).
15. M. Nakata, H. Nakatsuji, M. Ehara, M. Fukuda, K. Nakata, and K. Fujisawa, to be published.

16. P. Hohenberg and W. Kohn, *Phys. Rev.* **B 136**, 864 (1964).

17. H. Nakatsuji and R. G. Parr, *J. Chem. Phys.* **63**, 1112 (1975).

18. See also: S. T. Epstein and C. M. Rosenthal, *J. Chem. Phys.* **64**, 247 (1976).

19. Private communication from Prof. Mel Levy.

20. R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules*, Oxford Univ. Press, Oxford (1989).

21. H. Nakatsuji, *Phys. Rev.* **A14**, 41 (1976).

22. H. Nakatsuji, *Theor. Chem. Acc.* **102**, 97 (1999).

23. H. Nakatsuji, to be published.

24. L. Pauling and E. B. Wilson, Jr., *Introduction to Quantum Mechanics*, McGraw-Hill, New York (1935), p. 189.

25. S. Cho, *Sci. Rep. Gumma Univ.* **11**, 1 (1962).

26. L. Cohen and C. Frishberg, *Phys. Rev.* **A 13**, 927 (1976).

27. D. A. Mazziotti, *Phys. Rev.* **A 57**, 4219 (1998).

28. R. G. Parr, *J. Chem. Phys.* **40**, 3726 (1964).

29. S. T. Epstein, *Variation Method in Quantum Chemistry*, Academic, New York (1974).

30. H. Nakatsuji, *J. Chem. Phys.* **67**, 1312 (1977).

31. C. Valdemoro, in *Density Matrices and Density Functionals*, R. Erdahl and V. Smith (eds.), Reidel, Dordrecht (1987), p.275.

32. C. Valdemoro, *Phys. Rev.* **A 45**, 4462 (1992).

33. F. Colmenero, C. Perez del Valle, and C. Valdemoro, *Phys. Rev.* **A 47**, 971 (1993).

34. F. Colmenero and C. Valdemoro, *Phys. Rev.* **A 47**, 979 (1993).

35. F. Colmenero and C. Valdemoro, *Int. J. Quant. Chem.* **62**, 369 (1994).

36. C. Valdemoro, L. M. Tel, and E. Pérez-Romero, *Adv. Quant. Chem.* **28**, 33 (1997).

37. H. Nakatsuji and K. Yasuda, *Phys. Rev. Lett.* **76**, 1039 (1996).

38. K. Yasuda and H. Nakatsuji, *Phys. Rev.* **A 56**, 2648 (1997).

39. M. Nakata, M. Ehara, K. Yasuda, and H. Nakatsuji, *J. Chem. Phys.*, submitted.

40. A. A. Abrikosov, L. P. Gor'kov, and E. Dzyaloshinskii, *Methods of Quantum Field Theory in Statistical Physics*, Prentice-Hall, Englewood, Cliffs, NJ (1963).

41. D. A. Mazziotti, *Phys. Rev.* **A 60**, 3618 (1999).

42. H. Nakatsuji and K. Yasuda, unpublished.

43. J. M. Parks and R. G. Parr, *J. Chem. Phys.* **28**, 335 (1957).

44. H. Shall, *J. Chem. Phys.* **30**, 1405 (1959).

45. W. Kutzelnigg, *J. Chem. Phys.* **40**, 3640 (1964).

46. R. McWeeny and E. Steiner, *Adv. Quant. Chem.* **2**, 93 (1965).

47. E. Kapuy, *J. Chem. Phys.* **44**, 956 (1966).

48. A. J. Coleman, *Int. J. Quant. Chem.* **63**, 23 (1997).

49. P. R. Surján, *Topics in Current Chemistry*, **203**, 63 (1999).

50. D. T. Finkbeiner, Jr., *Introduction to Matrices and Linear Transformations*, W. H. Freeman and Co., San Francisco (1960).

51. M. Ehara, M. Nakata, H. Kou, K. Yasuda, and H. Nakatsuji, *Chem. Phys. Lett.* **305**, 483 (1999).

52. H. Nakatsuji and K. Hirao, *J. Chem. Phys.* **68**, 2053 (1978).

53. H. Nakatsuji, *Chem. Phys. Lett.* **59**, 362 (1978).

54. H. Nakatsuji, *Chem. Phys. Lett.* **67**, 329 (1978).

55. H. Nakatsuji, in *Computational Chemistry, Reviews of Current Trends*, J. Leszczynski (ed.), Vol. 2, World Scientific, Singapore (1996), p. 62.

56. T. Yonezawa, H. Nakatsuji, T. Kawamura, and H. Kato, *Chem. Phys. Lett.* **2**, 454 (1968).

57. H. Nakatsuji, H. Kato, and T. Yonezawa, *J. Chem. Phys.* **62**, 3175 (1969).

58. D. A. Mazziotti, *Chem. Phys. Lett.* **289**, 419 (1998).

59. D. A. Mazziotti, *Int. J. Quant. Chem.* **70**, 557 (1998).

60. K. Yasuda, *Phys. Rev.* **A 59**, 4133 (1999).

61. C. Valdemoro, *Int. J. Quant. Chem.* **60**, 131 (1996).

62. C. Valdemoro, M. P. de Lara-Castells, E. Pérez-Romero, and L. M. Tel, *Adv. Quant. Chem.* **31**, 37 (1999).

63. R. Kubo, *J. Phys. Soc. Jap.* **17**, 1100 (1962).

64. W. Kutzelnigg and D. Mukherjee, *J. Chem. Phys.* **110**, 2800 (1999).

65. W. Kutzelnigg and D. Mukherjee, *Chem. Phys. Lett.*, in press.

66. M. Levy, in *Density Matrices and Density Functionals*, R. Erdahl and V. Smith (eds.), Reidel, Dordrecht (1987), p.479.

67. J. Cioslowski and K. Pernal, *J. Chem. Phys.* **111**, 3396 (1999).