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# Simultaneous equations for calculating the pair density

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## Abstract

We propose a practical scheme for calculating the pair density (PD) on the basis of the density functional theory. In order to avoid the  $N$ -representability problem of the PD, we implement the variational principle within the set of PDs that are constructed from the single Slater determinants (SSDs). For the kinetic energy functional, we utilize the approximate form that is developed by means of the electron-coordinate scaling laws. The variational principle results in the simultaneous equations for constituent orbitals of the SSD. It yields the best one within the SSD-representable PDs.

## 1. Introduction

The pair density functional theory [1–6] is an attractive theory because the ground-state pair density (PD) has more information than the ground-state electron density [7, 8]. However, there are two problems for the practical use of the theory. One is concerned with the  $N$ -representability of the PD. The variational principle with respect to PD should be performed within the set of  $N$ -representable PDs. Although many attempts have been made to obtain necessary and sufficient conditions for  $N$ -representable PDs [9–18], they have not yet been obtained in a practical form. This is a long-standing problem. Another problem is concerned with an approximate form of the kinetic energy functional. As is well known, the exact kinetic energy cannot be expressed by the PD alone. Therefore, a certain approximation is needed for the kinetic energy functional. Several approximate forms have been proposed so far [19–22]. Recently, Levy and Aryers have proposed a formal method to avoid the above two problems simultaneously by using Lieb's Legendre transformation [23].

More recently, we have proposed an approximate scheme for calculating the ground-state PD by utilizing the extended constrained-search theory [24–31]. This is a computational approach that incorporates both of the above-mentioned problems. Namely, a noninteracting reference system is introduced so as to both ensure the  $N$ -representability of the reproduced PD and to provide the approximation of the kinetic energy functional [30].

In the present paper we shall present an alternative scheme for calculating the PD using the following strategies. For the  $N$ -representability problem, we adopt the same strategy as in previous work [30], that is to say the search area is fixed within the set of PDs which are constructed from the single Slater determinants (SSDs). (In what follows, we denote this set as  $C'$ .) The best solution is searched for within  $C'$ , regardless of whether the ground-state PD belongs to  $C'$  or not. The important point is that the best solution even in  $C'$  may include the correlation effect and is necessarily  $N$ -representable like the previous theory [30, 31]. This will be shown in the following sections.

For the development of the kinetic energy functional, we previously introduced the noninteracting reference system into the PD functional theory [30]. In the present scheme, we use the approximate form which has been derived from the scaling property of the kinetic energy functional. Due to the simple approximate form of the kinetic energy functional, the resultant simultaneous equations do not contain any differential operators. This feature is preferable in terms of computational accuracy and time.

Using the above strategies, we propose a computational scheme for calculating the PD. The organization of this paper is as follows. In section 2, we give the preliminary definitions of various quantities that will be required in the subsequent discussions. In section 3, the approximate form of the kinetic energy functional is derived by using the scaling property of the kinetic energy functional. In section 4, we give simultaneous equations for constituent orbitals of the SSD that yields the best PD. In section 5, merits of the present scheme are discussed from the viewpoint of the computation and the total energy. Finally, some concluding remarks are given in section 6.

## 2. Pair density functional theory

Let us begin with the overview of the PD functional theory. The Hamiltonian we shall consider is given by

$$\hat{H} = \hat{T} + \hat{W} + \int \hat{\rho}(\mathbf{r})v_{\text{ext}}(\mathbf{r}) d\mathbf{r}, \quad (1)$$

where  $\hat{T}$ ,  $\hat{W}$  and  $\hat{\rho}(\mathbf{r})$  are operators of the kinetic energy, electron–electron interaction and electron density, respectively, and  $v_{\text{ext}}(\mathbf{r})$  stands for the external potential. For this system, the Hohenberg–Kohn theorem holds by taking the PD as a basic variable. The PD is defined by

$$\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \langle \Psi | \hat{\gamma}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') | \Psi \rangle \quad (2)$$

with

$$\hat{\gamma}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \frac{1}{2} \int \int \hat{\psi}^+(\mathbf{r}, \eta) \hat{\psi}^+(\mathbf{r}', \eta') \hat{\psi}(\mathbf{r}', \eta') \hat{\psi}(\mathbf{r}, \eta) d\eta d\eta', \quad (3)$$

where  $\hat{\psi}(\mathbf{r}, \eta)$  and  $\hat{\psi}^+(\mathbf{r}, \eta)$  are field operators of electrons,  $\eta$  and  $\eta'$  are spin coordinates, and  $\Psi$  is the antisymmetric wavefunction. According to the constrained-search formulation of the PD functional theory, the universal functional  $F[\gamma^{(2)}]$  is defined by

$$F[\gamma^{(2)}] := \text{Min}_{\Psi \rightarrow \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle. \quad (4)$$

By using this definition, the Hohenberg–Kohn theorem can be proven in the extended form [1, 4, 30]. If the minimizing wavefunction in equation (4) is denoted by  $\Psi[\gamma^{(2)}]$ , then the theorem is expressed as

$$\Psi_0 = \Psi[\gamma_0^{(2)}] \quad (5)$$

and

$$\begin{aligned} E_0 &= \text{Min}_{\gamma^{(2)}} E[\gamma^{(2)}] \\ &= E[\gamma_0^{(2)}], \end{aligned} \quad (6)$$

where  $\Psi_0$ ,  $E_0$  and  $\gamma_0^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$  stand for the ground-state wavefunction, energy and pair density, respectively. Further,  $E[\gamma^{(2)}]$  is the total energy functional which is defined as

$$E[\gamma^{(2)}] := F[\gamma^{(2)}] + \frac{2}{N-1} \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') v_{\text{ext}}(\mathbf{r}) \, \mathbf{d}\mathbf{r} \, \mathbf{d}\mathbf{r}'. \quad (7)$$

By using the kinetic energy functional  $T[\gamma^{(2)}]$  which is defined by

$$T[\gamma^{(2)}] := \langle \Psi[\gamma^{(2)}] | \hat{T} | \Psi[\gamma^{(2)}] \rangle, \quad (8)$$

equation (7) is rewritten as

$$E[\gamma^{(2)}] = T[\gamma^{(2)}] + e^2 \iint \frac{\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \, \mathbf{d}\mathbf{r} \, \mathbf{d}\mathbf{r}' + \frac{2}{N-1} \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') v_{\text{ext}}(\mathbf{r}) \, \mathbf{d}\mathbf{r} \, \mathbf{d}\mathbf{r}'. \quad (9)$$

Equation (9) is the starting expression for the total energy functional in the PD functional theory. As mentioned in section 1, the approximate form of  $T[\gamma^{(2)}]$  should be given so as to perform the variational principle for equation (6).

### 3. Approximate form of the kinetic energy functional

In this section, we shall give an approximate form of  $T[\gamma^{(2)}]$ . For this purpose, we use the scaling property of  $T[\gamma^{(2)}]$  [20]. By using equation (4) and the fact that  $\Psi[\gamma^{(2)}]$  yields  $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ , equation (8) can be rewritten as [2, 20, 30]

$$T[\gamma^{(2)}] = \text{Min}_{\Psi \rightarrow \gamma^{(2)}} \langle \Psi | \hat{T} | \Psi \rangle. \quad (10)$$

From equation (10), the minimizing wavefunction  $\Psi[\gamma^{(2)}]$  can be obtained by minimizing  $\langle \Psi | \hat{T} | \Psi \rangle$  with two constraints, i.e.  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  yields a prescribed  $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ , and is normalized to unity. In accordance with the Lagrange undetermined multiplier method, we introduce the Lagrange multipliers  $\lambda[\gamma^{(2)}](\mathbf{r}, \mathbf{r}')$  and  $\bar{E}$  corresponding to the above constraints. Thus, we obtain the equation for  $\Psi[\gamma^{(2)}]$ :

$$\begin{aligned} & \left\{ \hat{T} + \iint \lambda[\gamma^{(2)}](\mathbf{r}, \mathbf{r}') \hat{\gamma}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') \, \mathbf{d}\mathbf{r} \, \mathbf{d}\mathbf{r}' \right\} \Psi[\gamma^{(2)}](\mathbf{r}_1, \dots, \mathbf{r}_N) \\ &= \bar{E} \Psi[\gamma^{(2)}](\mathbf{r}_1, \dots, \mathbf{r}_N). \end{aligned} \quad (11)$$

This equation leads to the scaling property of  $T[\gamma^{(2)}]$  [20, 30]. We have

$$T[\gamma_\zeta^{(2)}] = \zeta^2 T[\gamma^{(2)}], \quad (12)$$

where  $\zeta$  is a scaling factor for the electron coordinates, and  $\gamma_\zeta^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$  denotes the scaled PD that is given by

$$\gamma_\zeta^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \zeta^6 \gamma^{(2)}(\zeta \mathbf{r} \zeta \mathbf{r}'; \zeta \mathbf{r} \zeta \mathbf{r}'). \quad (13)$$

Letting  $\lim_{\zeta \rightarrow 1} \frac{\partial}{\partial \zeta}$  act on both sides of equation (12), and integrating by parts, we obtain

$$\begin{aligned} 2T[\gamma^{(2)}] &= - \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') \mathbf{r} \cdot \nabla \left\{ \frac{\delta T[\gamma^{(2)}]}{\delta \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')} \right\} \, \mathbf{d}\mathbf{r} \, \mathbf{d}\mathbf{r}' \\ &\quad - \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') \mathbf{r}' \cdot \nabla \left\{ \frac{\delta T[\gamma^{(2)}]}{\delta \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')} \right\} \, \mathbf{d}\mathbf{r} \, \mathbf{d}\mathbf{r}'. \end{aligned} \quad (14)$$

With reference to the local density approximation in the conventional density functional theory, the following approximate form of  $T[\gamma^{(2)}]$  is assumed

$$T[\gamma^{(2)}] = \iint t(\gamma^{(2)})|_{\gamma^{(2)}=\gamma^{(2)}(\mathbf{r}\mathbf{r}';\mathbf{r}\mathbf{r}')} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}', \quad (15)$$

where  $t(\gamma^{(2)})$  is a function of  $\gamma^{(2)}$ . Substituting equation (15) into equation (14), we get

$$\iint \left\{ 4t(\gamma^{(2)}) - 3\gamma^{(2)} \frac{\partial t(\gamma^{(2)})}{\partial \gamma^{(2)}} \right\} |_{\gamma^{(2)}=\gamma^{(2)}(\mathbf{r}\mathbf{r}';\mathbf{r}\mathbf{r}')} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}' = 0. \quad (16)$$

As the necessary condition, we get the differential equation with respect to  $t(\gamma^{(2)})$ :

$$4t(\gamma^{(2)}) - 3\gamma^{(2)} \frac{\partial t(\gamma^{(2)})}{\partial \gamma^{(2)}} = 0. \quad (17)$$

Solving the differential equation, and substituting the solution into equation (15), we finally get the approximate form of  $T[\gamma^{(2)}]$ :

$$T[\gamma^{(2)}] = C \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')^{4/3} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}', \quad (18)$$

where  $C$  is a constant. This approximate form is regarded as a special case of the approximate form that has been proposed by Levy and Ziesche [20]. In the following discussion, we use equation (18) as an approximate form of the kinetic energy functional.

#### 4. Simultaneous equations

The variational principle should be performed within  $N$ -representable PDs. However, the necessary and sufficient conditions for  $N$ -representable PDs have not yet been obtained as mentioned in section 1. In the present scheme, the search area is fixed within  $C'$  similarly to previous work [30]. The PD within  $C'$  is expressed as the expectation value of  $\hat{\gamma}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$  with respect to a SSD, i.e.,

$$\begin{aligned} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \frac{1}{2} \sum_{\mu_1, \mu_2} \left\{ \iint \psi_{\mu_1}^*(\mathbf{r}, \eta) \psi_{\mu_2}^*(\mathbf{r}', \eta') \psi_{\mu_2}(\mathbf{r}', \eta') \psi_{\mu_1}(\mathbf{r}, \eta) \, \mathrm{d}\eta \, \mathrm{d}\eta' \right. \\ \left. - \iint \psi_{\mu_1}^*(\mathbf{r}, \eta) \psi_{\mu_2}^*(\mathbf{r}', \eta') \psi_{\mu_1}(\mathbf{r}', \eta') \psi_{\mu_2}(\mathbf{r}, \eta) \, \mathrm{d}\eta \, \mathrm{d}\eta' \right\}, \end{aligned} \quad (19)$$

where  $\psi_{\mu}(\mathbf{r}, \eta)$ 's denote  $N$  orthonormal single-particle orbitals which construct the SSD. Since  $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$  is regarded as a functional of the set  $\{\psi_{\mu}(\mathbf{r}, \eta)\}$ , we can perform the variation of  $E[\gamma^{(2)}]$  with respect to the set  $\{\psi_{\mu}(\mathbf{r}, \eta)\}$  instead of  $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ . This variation enables us to perform the variational principle within  $C'$ . Consequently, the following functional of the set  $\{\psi_{\mu}(\mathbf{r}, \eta)\}$  should be minimized:

$$\Omega[\{\psi_{\mu}\}] = E[\gamma^{(2)}[\{\psi_{\mu}\}]] - \sum_{\mu, \nu} \varepsilon_{\mu\nu} \left\{ \int \psi_{\mu}^*(\mathbf{r}, \eta) \psi_{\nu}(\mathbf{r}, \eta) \, \mathrm{d}\mathbf{r} \, \mathrm{d}\eta - \delta_{\mu\nu} \right\}, \quad (20)$$

where  $\varepsilon_{\mu\nu}$  is the Lagrange multiplier which corresponds to the constraint

$$\int \psi_{\mu}^*(\mathbf{r}, \eta) \psi_{\nu}(\mathbf{r}, \eta) \, \mathrm{d}\mathbf{r} \, \mathrm{d}\eta = \delta_{\mu\nu}. \quad (21)$$

Substituting equations (9) and (18) into equation (20), we get

$$\Omega[\{\psi_{\mu}\}] = C \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')^{4/3} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}' + e^2 \iint \frac{\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}'$$

$$\begin{aligned}
& + \frac{1}{N-1} \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') \{v_{\text{ext}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}')\} \mathbf{d}\mathbf{r} \mathbf{d}\mathbf{r}' \\
& - \sum_{\mu, \nu} \varepsilon_{\mu\nu} \left\{ \int \psi_{\mu}^*(\mathbf{r}, \eta) \psi_{\nu}(\mathbf{r}, \eta) \mathbf{d}\mathbf{r} \mathbf{d}\eta - \delta_{\mu\nu} \right\}, \tag{22}
\end{aligned}$$

where we use the fact that  $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \gamma^{(2)}(\mathbf{r}'\mathbf{r}; \mathbf{r}'\mathbf{r})$  in the second line. The minimization condition  $\delta\Omega/\delta\psi_{\mu}^*(\mathbf{r}, \eta) = 0$  yields

$$\begin{aligned}
& \iint \sum_{\nu} \{ \psi_{\nu}^*(\mathbf{r}_1, \eta_1) \psi_{\nu}(\mathbf{r}_1, \eta_1) \psi_{\mu}(\mathbf{r}, \eta) - \psi_{\nu}^*(\mathbf{r}_1, \eta_1) \psi_{\mu}(\mathbf{r}_1, \eta_1) \psi_{\nu}(\mathbf{r}, \eta) \} \\
& \quad \times \left[ \frac{4C}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} + \frac{v_{\text{ext}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}_1)}{N-1} \right] \mathbf{d}\mathbf{r}_1 \mathbf{d}\eta_1 \\
& = \sum_{\nu} \varepsilon_{\mu\nu} \psi_{\nu}(\mathbf{r}, \eta). \tag{23}
\end{aligned}$$

The Lagrange multipliers  $\varepsilon_{\mu\nu}$  are shown to be elements of a Hermitian matrix  $\varepsilon$ . It is always possible, therefore, to find a unitary matrix  $U$  such that  $U^{-1}\varepsilon U$  becomes a diagonal matrix, i.e.

$$\sum_{i, j} U_{i\mu}^* \varepsilon_{ij} U_{j\nu} = \bar{\varepsilon}_{\mu} \delta_{\mu\nu}, \tag{24}$$

where  $\bar{\varepsilon}_{\mu}$  are diagonal elements of  $U^{-1}\varepsilon U$  and  $U_{j\nu}$  denote matrix elements of  $U$ .

Let us consider the new set of orbitals  $\{\chi_{\mu}(\mathbf{r}, \eta)\}$  that is obtained from the transformation  $\chi_{\mu}(\mathbf{r}, \eta) = \sum_i U_{i\mu}^* \psi_i(\mathbf{r}, \eta)$ . Since  $U$  is a unitary matrix, this transformation is rewritten as

$$\psi_{\mu}(\mathbf{r}, \eta) = \sum_{\nu} U_{\mu\nu} \chi_{\nu}(\mathbf{r}, \eta). \tag{25}$$

Substituting equation (25) into equations (21) and (23), and using equation (24), we finally get the following simultaneous equations for  $\{\chi_{\mu}(\mathbf{r}, \eta)\}$ :

$$\begin{aligned}
& \iint \sum_{\nu} \{ \chi_{\nu}^*(\mathbf{r}_1, \eta_1) \chi_{\nu}(\mathbf{r}_1, \eta_1) \chi_{\delta}(\mathbf{r}, \eta) - \chi_{\nu}^*(\mathbf{r}_1, \eta_1) \chi_{\delta}(\mathbf{r}_1, \eta_1) \chi_{\nu}(\mathbf{r}, \eta) \} \\
& \quad \times \left[ \frac{4C}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} + \frac{v_{\text{ext}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}_1)}{N-1} \right] \mathbf{d}\mathbf{r}_1 \mathbf{d}\eta_1 \\
& = \bar{\varepsilon}_{\delta} \chi_{\delta}(\mathbf{r}, \eta) \tag{26}
\end{aligned}$$

and

$$\int \chi_{\mu}^*(\mathbf{r}, \eta) \chi_{\nu}(\mathbf{r}, \eta) \mathbf{d}\mathbf{r} \mathbf{d}\eta = \delta_{\mu\nu}. \tag{27}$$

If we obtain the set  $\{\chi_{\mu}(\mathbf{r}, \eta)\}$  from the above equations, then the best solution in  $C'$  is provided by

$$\begin{aligned}
\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') & = \frac{1}{2} \sum_{\mu_1, \mu_2} \left\{ \iint \chi_{\mu_1}^*(\mathbf{r}, \eta) \chi_{\mu_2}^*(\mathbf{r}', \eta') \chi_{\mu_2}(\mathbf{r}', \eta') \chi_{\mu_1}(\mathbf{r}, \eta) \mathbf{d}\eta \mathbf{d}\eta' \right. \\
& \quad \left. - \iint \chi_{\mu_1}^*(\mathbf{r}, \eta) \chi_{\mu_2}^*(\mathbf{r}', \eta') \chi_{\mu_1}(\mathbf{r}', \eta') \chi_{\mu_2}(\mathbf{r}, \eta) \mathbf{d}\eta \mathbf{d}\eta' \right\}, \tag{28}
\end{aligned}$$

because the SSD is generally kept invariant under a unitary transformation (25) except for the trivial phase factor. Equations (26) and (27) should be solved simultaneously with equation (28).

## 5. Discussions

In this section, we shall discuss the merits of the present scheme from the viewpoint of the computation and the total energy. First, let us explain that simultaneous equations (26) and (27) are tractable for calculating the PD. For this aim, equation (26) is rewritten as

$$\{F(\mathbf{r}) - \bar{\varepsilon}_\delta\} \chi_\delta(\mathbf{r}, \eta) = G_\delta(\mathbf{r}, \eta) \chi_\delta(\mathbf{r}, \eta) \quad (29)$$

with

$$F(\mathbf{r}) = v_{\text{ext}}(\mathbf{r}) + \iint \sum_v |\chi_v(\mathbf{r}_1, \eta_1)|^2 \times \left\{ \frac{4C}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} + \frac{v_{\text{ext}}(\mathbf{r}_1)}{N-1} \right\} d\mathbf{r}_1 d\eta_1, \quad (30)$$

$$G_\delta(\mathbf{r}, \eta) = \iint \sum_v \{ \chi_v^*(\mathbf{r}_1, \eta_1) \chi_\delta(\mathbf{r}_1, \eta_1) \chi_v(\mathbf{r}, \eta) \} \times \left\{ \frac{4C}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} + \frac{v_{\text{ext}}(\mathbf{r}_1)}{N-1} \right\} d\mathbf{r}_1 d\eta_1, \quad (31)$$

where the orthonormality of  $\{\chi_\mu(\mathbf{r}, \eta)\}$  is used. The outline of the calculation procedure is as follows. Initially, a trial set of  $\{\chi_\mu(\mathbf{r}, \eta)\}$  is prepared so as to calculate  $F(\mathbf{r})$  and  $G_\delta(\mathbf{r}, \eta)$ . Then, the new  $\chi_\delta(\mathbf{r}, \eta)$  can be obtained from equation (29) for a given value of  $\bar{\varepsilon}_\delta$ . The value of  $\bar{\varepsilon}_\delta$  is determined by requiring  $\chi_\delta(\mathbf{r}, \eta)$  to be normalized, i.e. the value of  $\bar{\varepsilon}_\delta$  is changed until  $\chi_\delta(\mathbf{r}, \eta)$  is normalized to unity. After the determinations of all  $\chi_\delta(\mathbf{r}, \eta)$  and  $\bar{\varepsilon}_\delta$ , the convergence and orthogonality are checked appropriately. The iteration goes on until the convergence and orthogonality are accomplished. In this way, simultaneous equations can be solved in a self-consistent way. This procedure is quite similar to the calculation scheme of the Hartree–Fock equation [32]. The feature of these simultaneous equations is that they do not contain any differential operators. So, the present scheme has an advantage over the previous scheme [30, 31] from the viewpoint of computational accuracy and time.

Next, we shall show that searching within  $C'$  may provide the better result than the Hartree–Fock approximation. The minimization of  $E[\gamma^{(2)}]$  within  $C'$  can be rewritten as

$$\begin{aligned} \text{Min}_{\gamma^{(2)} \in C'} E[\gamma^{(2)}] &= \text{Min}_{\gamma^{(2)} \in C'} \left\{ F[\gamma^{(2)}] + \frac{2}{N-1} \iint \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') v_{\text{ext}}(\mathbf{r}) d\mathbf{r} d\mathbf{r}' \right\} \\ &= \text{Min}_{\gamma^{(2)} \in C'} \{ \text{Min}_{\Psi \rightarrow \gamma^{(2)}} \langle \Psi | H | \Psi \rangle \} \\ &= \text{Min}_{\Psi \in D'} \langle \Psi | H | \Psi \rangle, \end{aligned} \quad (32)$$

where  $D'$  is the set of wavefunctions that yield PDs of  $C'$ . The set  $D'$  contains not only all SSDs but also other types of wavefunctions [15]. Namely, the set of all SSDs  $\{\Phi\}$  is a subset of  $D'$ . Therefore, we obtain

$$\text{Min}_{\Psi \in D'} \langle \Psi | H | \Psi \rangle \leq \text{Min}_{\{\Phi\}} \langle \Phi | H | \Phi \rangle. \quad (33)$$

Substitution of equation (32) into equation (33) leads to the following inequality:

$$\text{Min}_{\gamma^{(2)} \in C'} E[\gamma^{(2)}] \leq \text{Min}_{\{\Phi\}} \langle \Phi | H | \Phi \rangle. \quad (34)$$

Note that  $\text{Min}_{\{\Phi\}} \langle \Phi | H | \Phi \rangle$  is equal to the total energy of the Hartree–Fock approximation. Taking into account the fact that the SSD-representable PD is necessarily  $N$ -representable, the above inequality means that searching within  $C'$  is superior to the Hartree–Fock approximation if we prepare the well-behaved form of the kinetic energy functional. Therefore, we conclude that the best PD within  $C'$  may include the correlation effect more or less, but definitely if equation (18) works well.

## 6. Concluding remarks

We shall comment on the search region  $C'$ . Since the necessary and sufficient conditions for the  $N$ -representable PDs have not yet been found, we cannot judge whether the set of the SSD-representable PDs is too small or not. No one knows to what extent the ground-state PD can be reproduced by using a SSD—this is still an open question. Concerning this problem, Davidson has pointed out that it is crucial how many linearly independent factors must be involved in the formal expansion for PDs [33]. His conclusion is that in any case the expansion must contain at least  $N$  linearly independent factors for a PD of an  $N$ -electron system [33]. Although the form of the SSD-representable PD intuitively seems to be restrictive, it is difficult to judge from his paper to what extent the SSD-representable PD can express the ground-state PD.

Thus, we may expect that searching for the best PD within  $C'$  would give a good approximation, while we also have the negative possibility such that the search region would be much smaller than the set of  $N$ -representable PDs. In spite of the fact that such a negative possibility is uncertain at present, some workers may be sceptical that the search region would be too small. This may be due to the fact that the correlation effects are caused by the doubly excited determinants which differ from the Hartree–Fock determinant in replacing a couple of occupied states by a couple of unoccupied ones. This picture is based on the configuration interaction (CI) method, and the constituent single-particle orbitals of the determinants are the solution of the Hartree–Fock equation. However, the Kohn–Sham orbital is essentially different from the Hartree–Fock orbital. The SSD can exactly reproduce the ground-state electron density in the density function theory [34], while the Hartree–Fock never reproduces it.

Against such a background, we shall position the present scheme in the PD functional theory. The PD functional theory is not yet a fully formed field. Therefore, it is important as a first step in developing the PD functional theory to present an initial standard scheme which corresponds to the Hartree–Fock approximation of the wavefunction theory. The position of the present scheme in the PD functional theory just corresponds to that of the Hartree–Fock approximation in the wavefunction theory. As is well known, the Hartree–Fock approximation gives the best solution within the set of SSDs. In a similar way to that, the present scheme gives the best PD within the restricted search region consisting of the SSD-representable PDs. There is no doubt that the Hartree–Fock approximation can be regarded as an initial standard scheme in the wavefunction theory. Correspondingly, the present scheme may be regarded as an initial standard in the PD functional theory. Furthermore, although the search region is restricted, the present scheme may contain the correlation effects more or less. This fact is also the reason why the present scheme may be regarded as an initial standard scheme in the PD functional theory.

Therefore, it seems to be meaningful to check the performance of the present scheme. We are sure that this performance evaluation is the first thing to be done to give the starting point of the PD functional theory similarly to the Hartree–Fock approximation of the wavefunction theory. We are now preparing numerical calculations for this purpose.

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