

Pair density-functional theory by means of the correlated wave function

Masahiko Higuchi

Department of Physics, Faculty of Science, Shinshu University, Matsumoto 390-8621, Japan

Katsuhiko Higuchi

Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8527, Japan

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We present a density-functional scheme for calculating the pair density (PD) by means of the correlated wave function. The Jastrow wave function is adopted as the correlated wave function. By using the lowest-order approximation to the Jastrow wave function PDs, the search region for the ground-state PD is substantially extended as compared with our previous theory [*Physica B* **387**, 117 (2007)]. The variational principle results in simultaneous equations that are practicable to calculate the ground-state PD.

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I. INTRODUCTION

The pair density (PD) functional theory has recently attracted particular interest because it provides the obvious way to improve on density-functional theory (DFT) [1–9]. Ziesche first proposed the PD functional theory about a decade ago [1,2], and then many workers followed his work and have developed a variety of approaches [3–9].

Very recently, we have proposed an approximate scheme for calculating the PD on the basis of the extended constrained-search theory [10–14]. By introducing a noninteracting reference system [10,11], the resultant PD corresponds to the best solution within the set of PDs that are constructed from a single Slater determinant (SSD). This PD functional theory has two kinds of merit. The first is that the reproduced PD is necessarily N -representable. This is a strong merit because the necessary and sufficient conditions for the N -representable PD are not yet known [15–26]. The second merit is the tractable form of the kinetic energy functional. The kinetic energy functional cannot exactly be written by using the PD alone. Some approximation is required [7]. In this theory, we have successfully given an approximate form of the kinetic energy functional with the aid of the coordinate scaling of electrons [10,11].

On the other hand, a significant problem remains in that approach [10]; namely, there exists the possibility that the solution might be far from the correct value of the ground-state PD. This is because the search region of the PDs may be smaller than the set of N -representable PDs. In order to improve the PD functional theory, we have to extend the search region of the PDs to the set of N -representable PDs as closely as possible. At least, we had better extend the search region beyond the set of SSD-representable PDs [27].

In this paper, we shall employ the strategy for reproducing the PDs not by means of the SSD, but through the correlated wave function. As the correlated wave function, we adopt the Jastrow wave function that is defined as the SSD multiplied by the correlation function [28–34]. Owing to the correlation function, the search region becomes substantially larger than the set of the SSD-representable PDs.

The organization of this paper is as follows. In Sec. II, we provide the preliminary definitions of various quantities that appear in the following sections. In Sec. III, by means of the

variational principle with respect to the PD, we derive simultaneous equations that yield the best PD within the Jastrow wave function PDs of lowest order. Such equations are quite tractable; the computational method for them is also proposed in Sec. III.

II. PRELIMINARY DEFINITIONS IN THE PD FUNCTIONAL THEORY

In this section we give the preliminary definitions that will be used in the present scheme. The PD is defined as the diagonal elements of the spinless second-order reduced density matrix, i.e.,

$$\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \langle \Psi | \frac{1}{2} \int \int \hat{\psi}^\dagger(\mathbf{r}, \eta) \hat{\psi}^\dagger(\mathbf{r}', \eta') \hat{\psi}(\mathbf{r}', \eta') \times \hat{\psi}(\mathbf{r}, \eta) d\eta d\eta' | \Psi \rangle, \quad (1)$$

where $\hat{\psi}(\mathbf{r}, \eta)$ and $\hat{\psi}^\dagger(\mathbf{r}, \eta)$ are the field operators of the electrons, Ψ is the antisymmetric wave function, and \mathbf{r} and η are spatial and spin coordinates, respectively. We shall consider a system, the Hamiltonian of which is given by

$$\hat{H} = \hat{T} + \hat{W} + \int d\mathbf{r} \hat{\rho}(\mathbf{r}) v_{ext}(\mathbf{r}), \quad (2)$$

where \hat{T} , \hat{W} , and $\hat{\rho}(\mathbf{r})$ are operators of the kinetic energy, electron-electron interaction, and electron density, respectively, and $v_{ext}(\mathbf{r})$ stands for the external potential. In a similar way to the extended constrained-search theory [12–14], the universal functional is defined as

$$F[\gamma^{(2)}] = \underset{\Psi \rightarrow \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')}{\text{Min}} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle \\ = \langle \Psi[\gamma^{(2)}] | \hat{T} + \hat{W} | \Psi[\gamma^{(2)}] \rangle, \quad (3)$$

where $\Psi \rightarrow \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ denotes the searching over all antisymmetric wave functions that yield a prescribed $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$. In the second line, the minimizing wave function is expressed as $\Psi[\gamma^{(2)}]$. By using Eq. (3), the Hohenberg-Kohn theorems for the PD functional theory can be easily proved [1,5]. Here we show only their results [10]:

$$\Psi_0 = \Psi[\gamma_0^{(2)}] \quad (4)$$

and

$$\begin{aligned} E_0 &= \text{Min}_{\gamma^{(2)}} E[\gamma^{(2)}] \\ &= E[\gamma_0^{(2)}], \end{aligned} \quad (5)$$

where Ψ_0 , E_0 , and $\gamma_0^{(2)}$ are the ground-state wave function, ground-state energy, and ground-state PD, respectively, and where $E[\gamma^{(2)}]$ is the total energy functional that is given by

$$E[\gamma^{(2)}] = F[\gamma^{(2)}] + \frac{2}{N-1} \int \int d\mathbf{r} d\mathbf{r}' v_{ext}(\mathbf{r}) \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}'). \quad (6)$$

Equations (4) and (5) correspond to the first and second Hohenberg-Kohn theorems, respectively. Let us suppose that

$$T[\gamma^{(2)}] = \langle \Psi[\gamma^{(2)}] | \hat{T} | \Psi[\gamma^{(2)}] \rangle; \quad (7)$$

then Eq. (6) is rewritten as

$$\begin{aligned} E[\gamma^{(2)}] &= T[\gamma^{(2)}] + e^2 \int \int d\mathbf{r} d\mathbf{r}' \frac{\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \\ &\quad + \frac{2}{N-1} \int \int d\mathbf{r} d\mathbf{r}' v_{ext}(\mathbf{r}) \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}'), \end{aligned} \quad (8)$$

where, in the second term, we use the fact that the expectation value of \hat{W} is exactly written in terms of $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$. Equation (8) is the starting expression for the total energy functional in the PD functional theory.

As mentioned in Sec. I, the kinetic energy of the PD functional theory cannot be exactly expressed by the PDs alone. In other words, we have to employ the approximate form. So far, the kinetic energy functional of the PD functional theory has been developed by several workers [10,35,36]. In this paper, we make use of an approximate form of the kinetic energy functional which has been derived by utilizing the scaling property of the kinetic energy functional [10,36]. The explicit form is given by

$$T[\gamma^{(2)}] = K \int \int d\mathbf{r} d\mathbf{r}' \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')^{4/3}, \quad (9)$$

where K is an arbitrary constant.

III. SINGLE-PARTICLE EQUATIONS

Equation (5) corresponds to the variational principle with respect to the PD. The search region of the PDs should be of course within the set of N -representable PDs. In order to make the search region close to the set of N -representable PDs, we shall introduce the search region of the PDs that is approximately calculated from the correlated wave functions. The search region is substantially extended as compared with the previous theory [10], because it is restricted within the set of SSD-representable PDs. Extension of the search region can be regarded as one of appropriate developments of the PD functional theory [27].

In this paper we adopt the Jastrow wave function as the correlated wave function. The explicit evaluation of the PD using the Jastrow wave function is actually very hard [28–34]. As a consequence, the approximation technique to evaluate the PD has been developed [28–34]. The expectation value of the PD operator with respect to the Jastrow wave function can be systematically expressed with the aid of the Yvon-Mayer diagrammatic technique [28,29]. Here we shall use the lowest-order approximation of the expectation value of the PD operator.

The Jastrow wave function is defined as [28,29]

$$\Psi_J(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{C_N}} \prod_{1 \leq i < j \leq N} f(r_{ij}) \Phi_{SSD}(x_1, x_2, \dots, x_N), \quad (10)$$

where $\Phi_{SSD}(x_1, x_2, \dots, x_N)$ is the SSD, $f(r_{ij}) = f(|\mathbf{r}_i - \mathbf{r}_j|)$ is the correlation function, and C_N is the normalization constant. Suppose that the correlation function is chosen to satisfy the cusp condition for the antisymmetric wave function. The lowest-order approximation for the expectation value of the PD operator is given by [28]

$$\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = |f(|\mathbf{r} - \mathbf{r}'|)|^2 \gamma_{SSD}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}'), \quad (11)$$

where $\gamma_{SSD}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ is the expectation value of the PD operator with respect to the SSD. Supposing N orthonormal spin orbitals of the SSD are denoted as $\{\psi_\mu(x)\}$, then Eq. (11) is explicitly expressed as

$$\begin{aligned} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') &= \frac{1}{2} |f(|\mathbf{r} - \mathbf{r}'|)|^2 \sum_{\mu_1, \mu_2=1}^N \int \int d\eta d\eta' \\ &\quad \times \{ \psi_{\mu_1}^*(x) \psi_{\mu_2}^*(x') \psi_{\mu_1}(x) \psi_{\mu_2}(x') \\ &\quad - \psi_{\mu_1}^*(x) \psi_{\mu_2}^*(x') \psi_{\mu_2}(x) \psi_{\mu_1}(x') \}. \end{aligned} \quad (12)$$

Next, let us consider the variational principle with respect to the PD, i.e., Eq. (5). The variation of the PD is performed via the spin orbitals of Eq. (12) with the restriction that they are orthonormal to each other. Using the Lagrange method of undetermined multipliers, we minimize the following functional without the restriction:

$$\Omega[\{\psi_\mu\}] = E[\gamma^{(2)}] - \sum_{\mu, \nu} \varepsilon_{\mu\nu} \left\{ \int \psi_\mu^*(x) \psi_\nu(x) dx - \delta_{\mu\nu} \right\}, \quad (13)$$

where Eqs. (8), (9), and (12) are used in the first term on the right-hand side. The minimizing condition $\delta\Omega[\{\psi_\mu\}] = 0$ immediately leads to

$$\begin{aligned} \sum_\nu \int dx_1 \{ \psi_\nu^*(x_1) \psi_\nu(x_1) \psi_\mu(x) - \psi_\nu^*(x_1) \psi_\nu(x) \psi_\mu(x_1) \} \\ \times |f(|\mathbf{r} - \mathbf{r}_1|)|^2 \left(\frac{4K}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} \right) \\ + \frac{1}{N-1} [v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}_1)] = \sum_\nu \varepsilon_{\mu\nu} \psi_\nu(x), \end{aligned} \quad (14)$$

where the chain rule for the functional derivatives is utilized. The Lagrange multipliers $\varepsilon_{\mu\nu}$ should be determined by requiring that the spin orbitals are orthonormal to each other. In a similar way to the previous theory [10], we can simplify the above equations by means of a unitary transformation of the spin orbitals. Clearly $\varepsilon_{\mu\nu}$ is Hermitian; hence there exists $U_{\mu\nu}$ such that $\sum_{i,j} U_{i\mu}^* \varepsilon_{ij} U_{j\nu} = \tilde{\varepsilon}_{\mu} \delta_{\mu\nu}$ and the spin orbitals therefore can be transformed as

$$\psi_{\mu}(x) = \sum_{\nu} U_{\mu\nu} \chi_{\nu}(x). \quad (15)$$

Substituting Eq. (15) into Eq. (14), we obtain

$$\begin{aligned} & \sum_{\nu} \int dx_1 \{ \chi_{\nu}^*(x_1) \chi_{\nu}(x_1) \chi_{\mu}(x) - \chi_{\nu}^*(x_1) \chi_{\nu}(x) \chi_{\mu}(x_1) \} \\ & \times |f(|\mathbf{r} - \mathbf{r}_1|)|^2 \left(\frac{4K}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} \right. \\ & \left. + \frac{1}{N-1} [v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}_1)] \right) = \tilde{\varepsilon}_{\mu} \chi_{\mu}(x) \end{aligned} \quad (16)$$

with

$$\int \chi_{\mu}^*(x) \chi_{\nu}(x) dx = \delta_{\mu\nu}. \quad (17)$$

Direct substitution

$$\begin{aligned} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') &= \frac{1}{2} |f(|\mathbf{r} - \mathbf{r}'|)|^2 \sum_{\mu_1, \mu_2=1}^N \int \int d\eta d\eta' \\ & \times \{ \chi_{\mu_1}^*(x) \chi_{\mu_2}^*(x') \chi_{\mu_1}(x) \chi_{\mu_2}(x') \\ & - \chi_{\mu_1}^*(x) \chi_{\mu_2}^*(x') \chi_{\mu_2}(x) \chi_{\mu_1}(x') \} \end{aligned} \quad (18)$$

shows that $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ is invariant under the transformation U . Equations (16) and (17) are simultaneous equations, and the solutions yield the best PD within the set of PDs that are calculated from Eq. (18).

Our previous work is a proposal of a computational approach that deals with problems related to PD functional theory [10]. The present scheme is also a computational approach, and further improves on the previous theory concerning the search region of the PDs. In that sense, it would be useful to consider a computational procedure for solving the simultaneous equations (16) and (17).

The procedure proposed here is similar to that of the Hartree-Fock equation [37]. In order to make the computational procedure readily comprehensible, let us rewrite Eq. (16) as

$$\{F(\mathbf{r}) - \tilde{\varepsilon}_{\delta}\} \chi_{\delta}(x) = G_{\delta}(x) \quad (19)$$

with

$$\begin{aligned} F(\mathbf{r}) &= \int dx_1 |f(|\mathbf{r} - \mathbf{r}_1|)|^2 \sum_{\nu=1}^N |\chi_{\nu}(x_1)|^2 \left(\frac{4K}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} \right. \\ & \left. + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} + \frac{1}{N-1} [v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}_1)] \right), \end{aligned} \quad (20)$$

$$\begin{aligned} G_{\delta}(x) &= \int dx_1 |f(|\mathbf{r} - \mathbf{r}_1|)|^2 \left(\sum_{\nu=1}^N \chi_{\nu}^*(x_1) \chi_{\delta}(x_1) \chi_{\nu}(x) \right) \\ & \times \left(\frac{4K}{3} \gamma^{(2)}(\mathbf{r}\mathbf{r}_1; \mathbf{r}\mathbf{r}_1)^{1/3} + \frac{e^2}{|\mathbf{r} - \mathbf{r}_1|} \right. \\ & \left. + \frac{1}{N-1} [v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}_1)] \right), \end{aligned} \quad (21)$$

where the spin orbital $\chi_{\delta}(x)$ is the solution of Eq. (19), and should be determined in a self-consistent way. Here, note that the right-hand side of Eq. (19) comes from the second term of Eq. (18), and explicitly depends on the spin orbital $\chi_{\delta}(x)$. The key point to get the self-consistent solution is that spin orbitals of the previous iteration are used in calculating $F(\mathbf{r})$ and $G_{\delta}(x)$ [37]. By solving simultaneously Eqs. (17) and (19) with this technique, we can get a new set of spin orbitals and energy parameters $\tilde{\varepsilon}_{\delta}$. We continue this procedure until self-consistency for the solutions is accomplished [37].

At the end of this section, we shall give a brief comment on the N -representability of the PDs that are given by Eq. (18). The necessary and sufficient conditions for PDs to be N -representable have not yet been revealed. So it is acceptable to carry out the variational calculations with some necessary conditions imposed on the PDs, as in previous works [38–43]. It can be confirmed that the PDs of Eq. (18) satisfy four kinds of necessary conditions [44]. In this sense, we can say that the PDs are “approximately N -representable” as in the previous works [38–43]. Thus, it may be expected that the PD obtained in the present scheme is not too bad. Further, there is the possibility that the N -representability problem is reduced to the conditions imposed on the correlation function. Indeed, for a two-particle system ($N=2$), the PDs of Eq. (18) become N -representable if the correlation function is chosen appropriately [29]. It is a future issue to reveal what conditions should be imposed on the correlation function so as to allow the PDs for N -particle systems ($N \geq 3$) be N -representable.

IV. CONCLUDING REMARKS

In this paper, we propose the PD functional theory that yields the best PD within the set of Jastrow wave function PDs of the lowest order. Compared to the previous theory [10,11], the present one has the following features.

(1) The search region of the PDs is certainly larger than that of the previous theory [10]. In addition to that, the resultant PD is at least approximately N -representable. Therefore, it may be expected that the appropriate PD is obtained in the present scheme.

(2) Next we shall consider the present scheme from the viewpoint of the total energy. If the correlation function is chosen to be unity, then the present theory is reduced to the previous one exactly. It has already been proved that the total energy of the previous theory is better than that of the Hartree-Fock approximation [11]. If the correlation function is chosen most appropriately, then the search region is substantially equivalent to the set of PDs that are calculated by

varying both the correlation function and spin orbitals in Eq. (18). Therefore, the total energy of the present scheme is necessarily lower than in the previous one [10], and, needless to say, than that of the Hartree-Fock approximation.

(3) In addition to the above features, the present scheme has a feature that deserves special emphasis. Due to the fact that the PD functional theory is still a developing field, there hardly exist any computational approaches so far. Our previous paper proposed a computational approach that addresses both major problems of PD functional theory [10,11]. The present scheme is also a computational approach. The resultant simultaneous equations are quite tractable, as were the previous ones [10,11]. Also from such a viewpoint the present scheme seems to be valuable.

The next step is to perform the actual calculations so as to confirm to what extent the present scheme covers the N -representable PDs.

Finally, we would like to comment on the future prospects of the present theory. Although the present scheme utilizes the lowest-order approximation of the expectation value of the PD operator, the higher-order corrections can proceed systematically with the aid of the Yvon-Mayer diagrams [28,29]. Of course, it is anticipated that the equations will become more complicated. But, from the methodological point of view, it is important that the theoretical framework has the potential to improve the approximation systematically.

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