Pair density functional theory by means of the correlated wave function

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Abstract

We present a density functional scheme for calculating the pair density (PD) by means of the correlated wave function. This scheme is free from both of problems related to PD functional theory, i.e., (a) the need to constrain the variational principle to \( N \)-representable PDs and (b) the development of a kinetic energy functional. By using the correlated wave function, the searching region for the ground-state PD is substantially extended as compared with our previous theory[Physica B 372 (2007), in press]. The variational principle results in the simultaneous equations that yield the best PD beyond the previous theory, not to mention the Hartree-Fock approximation.

Note: The previous paper [Physica B 372 (2007), in press] can be downloaded from “Article in press” in the website of Physica B.
I. INTRODUCTION

The pair density (PD) functional theory has recently attracted particular interest because it provides the obvious way to improve on the density functional theory (DFT). Ziesche first proposed the PD functional theory about a decade ago, and then many workers followed his work and have developed a variety of approaches. Very recently, we have proposed an approximate scheme for calculating the PD on the basis of the extended constrained-search theory. By introducing the noninteracting reference system, the resultant PD corresponds to the best solution within the set of the PDs that are constructed from the single Slater determinant (SSD). This PD functional theory has two kinds of merits. The first one 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 have not yet been known. 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 to be introduced. In this theory, we have successfully given an approximate form of the kinetic energy functional with the aid of the coordinate scaling of electrons.

On the other hand, we also have the remaining problem in it. Namely, there exists the possibility that the solution might be far from the correct value of the ground-state PD. This is because the searching region of the PDs may be smaller than the set of $N$-representable PDs. In order to improve the PD functional theory with keeping the above-mentioned merits, we have to extend the searching region of the PDs to the set of $N$-representable PDs as closely as possible. At least, we had better extend the searching region beyond the set of the SSD-representable PDs.

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. Owing to the correlation function, the searching region substantially becomes larger than the set of the SSD-representable PDs. Of course, the reproduced PD is kept $N$-representable because the PD is calculated via the Jastrow wave function that is a kind of antisymmetric wave functions. Also the second merit is not missed in the present
scheme by utilizing the result of the scaling property of the kinetic energy functional.

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 that is superior to the previous one[10]. Such equations are quite tractable, the computational method of which are also proposed in Sec. III.

II. PRELIMINARY DEFINITIONS IN THE PD FUNCTIONAL THEORY

In this section we give the preliminary definitions which 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.,

$$\gamma^{(2)}(rr'; rr') = \langle \Psi | \frac{1}{2} \int \hat{\psi}^+(r, \eta) \hat{\psi}^+(r', \eta') \hat{\psi}(r', \eta') \hat{\psi}(r, \eta) d\eta' d\eta | \Psi \rangle,$$  \hspace{1cm} (1)

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

$$\hat{H} = \hat{T} + \hat{W} + \int dr \hat{\rho}(r) v_{ext}(r),$$  \hspace{1cm} (2)

where $\hat{T}$, $\hat{W}$ and $\hat{\rho}(r)$ are operators of the kinetic energy, electron-electron interaction and electron density, respectively, and $v_{ext}(r)$ stands for the external potential. In the similar way to the extended constrained-search theory[12, 13, 14], the universal functional is defined as

$$F[\gamma^{(2)}] = \operatorname{Min}_{\Psi \rightarrow \gamma^{(2)}(rr'; rr')} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle = \langle \Psi[\gamma^{(2)}] | \hat{T} + \hat{W} | \Psi[\gamma^{(2)}] \rangle,$$  \hspace{1cm} (3)

where $\Psi \rightarrow \gamma^{(2)}(rr'; rr')$ denotes the searching over all antisymmetric wave functions that yield a prescribed $\gamma^{(2)}(rr'; rr')$. 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]:

$$\Psi_0 = \Psi[\gamma_0^{(2)}],$$  \hspace{1cm} (4)
and

\[ E_0 = \min_{\gamma^{(2)}} E[\gamma^{(2)}] \]
\[ = E[\gamma^{(2)}_0], \]  

(5)

where \( \Psi_0, E_0 \) and \( \gamma^{(2)}_0 \) 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

\[ E[\gamma^{(2)}] = F[\gamma^{(2)}] + \frac{2}{N-1} \iint \! \! dr \! \! dr' v_{ext}(r) \gamma^{(2)}(rr'; rr'). \]  

(6)

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

\[ T[\gamma^{(2)}] = \langle \Psi[\gamma^{(2)}] | T | \Psi[\gamma^{(2)}] \rangle, \]

(7)

then Eq. (6) is rewritten as

\[ E[\gamma^{(2)}] = T[\gamma^{(2)}] + e^2 \iint \! \! dr \! \! dr' \frac{\gamma^{(2)}(rr'; rr')}{|r-r'|} + \frac{2}{N-1} \iint \! \! dr \! \! dr' v_{ext}(r) \gamma^{(2)}(rr'; rr'), \]

(8)

where, in the second term, we use the fact that the expectation value of \( \hat{W} \) is exactly written in terms of \( \gamma^{(2)}(rr'; rr') \). 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 in Eq. (8). So far, the kinetic energy functional of the PD functional theory has been developed by several workers \[10, 30, 31\]. 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 \[10, 31\]. The explicit form is given by

\[ T[\gamma^{(2)}] = K \iint \! \! dr \! \! dr' \gamma^{(2)}(rr'; rr')^{\frac{2}{3}}, \]

(9)

where \( K \) is an arbitrary constant.

### III. SINGLE-PARTICLE EQUATIONS

Equation (5) corresponds to the variational principle with respect to the PD. The searching region of the PDs should be of course within the set of \( N \)-representable PDs. For that
purpose, we shall introduce the searching region of the PDs that are calculated from the correlated wave functions. The searching 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 searching 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, 29]. As a consequence, the approximation technique to evaluate the PD has been developed especially in the field of nuclear physics. 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

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

(10)

where $\Phi_{SSD}(x_1, x_2, \cdots, x_N)$ is the SSD, and where $f(r_{ij}) = f(|r_i - r_j|)$ is the correlation function, and where $C_N$ 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

$$
\gamma^{(2)}(rr'; rr') = |f(|r - r'|)|^2 \gamma^{(2)}_{SSD}(rr'; rr'),
$$

(11)

where $\gamma^{(2)}_{SSD}(rr'; rr')$ 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

$$
\gamma^{(2)}(rr'; rr') = \frac{1}{2} |f(|r - r'|)|^2 \sum_{\mu_1, \mu_2 = 1}^{N} \int \int d\eta d\eta' \left\{ \psi_{\mu_1}^*(x) \psi_{\mu_2}^*(x') \psi_{\mu_1}(x) \psi_{\mu_2}(x') 
- \psi_{\mu_1}^*(x) \psi_{\mu_2}^*(x') \psi_{\mu_2}(x) \psi_{\mu_1}(x') \right\}.
$$

(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:

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

(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

\[
\sum_\nu \int d_1 \left\{ \psi_\nu^*(x) \psi_\nu(x) \psi_\mu(x) - \psi_\nu^*(x) \psi_\nu(x) \psi_\mu(x) \right\}
\times |f (|r - r_1|)|^2 \left\{ \frac{4K}{3} \gamma^{(2)}(rr_1; rr_1) \right\}^3 + \frac{e^2}{|r - r_1|} + \frac{1}{N - 1} \left( v_{\text{ext}}(r) + v_{\text{ext}}(r_1) \right) \right\}
= \sum_\nu \varepsilon_{\mu \nu} \psi_\nu(x),
\]

(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:

\[
\int \psi_\mu^*(x) \psi_\nu(x) dx = \delta_{\mu \nu}.
\]

(15)

In the similar way to the previous theory[10], we can simplify the above equations by means of a unitary transformation of the spin orbitals. It is easily shown that \( \varepsilon_{\mu \nu} \) forms the Hermitian matrix. Suppose that the unitary matrix which diagonalizes \( \varepsilon_{\mu \nu} \) is written by \( U_{\mu \nu} \), then

\[
\sum_{i,j} U_{i \mu}^* \varepsilon_{i j} U_{j \nu} = \tilde{\varepsilon}_{\mu} \delta_{\mu \nu}
\]

(16)

is satisfied, where \( \tilde{\varepsilon}_{\mu} \) is the diagonal element of the diagonal matrix. Let us consider the following transformation of the spin orbitals:

\[
\psi_\mu(x) = \sum_\nu U_{\mu \nu} \chi_\nu(x).
\]

(17)

Substituting Eq. (17) into Eq. (14), and using Eq. (16), we obtain

\[
\sum_\nu \int d_1 \left\{ \chi_\nu^*(x) \chi_\nu(x) \chi_\mu(x) - \chi_\nu^*(x) \chi_\nu(x) \chi_\mu(x) \right\}
\times |f (|r - r_1|)|^2 \left\{ \frac{4K}{3} \gamma^{(2)}(rr_1; rr_1) \right\}^3 + \frac{e^2}{|r - r_1|} + \frac{1}{N - 1} \left( v_{\text{ext}}(r) + v_{\text{ext}}(r_1) \right) \right\}
= \tilde{\varepsilon}_{\mu} \chi_\mu(x).
\]

(18)

Also, Eq. (15) is transformed into

\[
\int \chi_\mu^*(x) \chi_\nu(x) dx = \delta_{\mu \nu}.
\]

(19)

Here note that the expression for \( \gamma^{(2)}(rr'; rr'') \) in Eq. (13) is kept invariant under the unitary transformation. This is confirmed by substituting Eq. (17) into Eq. (12), i.e.,

\[
\gamma^{(2)}(rr'; rr'') = \frac{1}{2} |f (|r - r'|)|^2 \sum_{\mu_1, \mu_2 = 1}^N \int d\eta d\eta' \left\{ \chi_{\mu_1}^*(x) \chi_{\mu_2}^*(x') \chi_{\mu_1}(x) \chi_{\mu_2}(x') \right.
- \chi_{\mu_1}^*(x) \chi_{\mu_2}^*(x') \chi_{\mu_1}(x) \chi_{\mu_2}(x') \left\}
\]

(20)
Equations (18) and (19) are the simultaneous equations, and the solutions yield the best PD within the set of PDs that are calculated from Eq. (20).

Our previous work may be the first proposal of a computational approach that deals with problems related to the PD functional theory \[10\]. The present scheme is also a computational approach, and further improves on the previous theory concerning the searching region of the PDs. In that sense, it would be useful to consider a computational procedure for solving the simultaneous equations (18) and (19).

The procedure proposed here is similar to that of the Hartree-Fock equation \[32\]. In order to make the computational procedure readily comprehensible, let us rewrite Eq. (18) as

\[
\{F(r) - \tilde{\varepsilon}_\delta\} \chi_\delta(x) = G_\delta(x) \tag{21}
\]

with

\[
F(r) = \int dx_1 |f(|r - r_1|)|^2 \sum_{\nu=1}^{N} |\chi_\nu(x_1)|^2 \\
\times \left\{ \frac{4K}{3} \gamma^2 \rho_{\gamma_{1}\gamma_{1}} \frac{1}{r - r_1} + \frac{e^2}{|r - r_1|} + \frac{1}{N-1} (v_{ext}(r) + v_{ext}(r_1)) \right\}, \tag{22}
\]

\[
G_\delta(x) = \int dx_1 |f(|r - r'|)|^2 \left( \sum_{\nu=1}^{N} \chi^*_\nu(x_1) \chi_\delta(x_1) \chi_\nu(x) \right) \\
\times \left\{ \frac{4K}{3} \gamma^2 \rho_{\gamma_{1}\gamma_{1}} \frac{1}{r - r_1} + \frac{e^2}{|r - r_1|} + \frac{1}{N-1} (v_{ext}(r) + v_{ext}(r_1)) \right\}, \tag{23}
\]

where the spin orbital \(\chi_\delta(x)\) is the solution of Eq. (21), and should be determined in a self-consistent way. Here note that the right-hand side of Eq. (21) comes from the second term of Eq. (20), 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 \(F(r)\) and \(G_\delta(x)\) \[32\]. By solving simultaneously Eqs. (19) and (21) with this technique, we can get a new set of spin orbitals and energy parameters \(\tilde{\varepsilon}_\delta\)'s. We continue such a procedure until the self-consistency for the solutions is accomplished \[32\].

IV. CONCLUDING REMARKS

In this paper, we propose the PD functional theory that yields the best PD within the set of PDs that are constructed from the correlated wave functions. Compared to the previous one \[10, 11\], the present theory has the following features.
1. The present theory is superior to the previous one in that the searching region of the PDs is certainly larger than the set of SSD-representable PDs without missing the merits of the previous theory\[10\]. This means that the resultant PD is more reasonable than that of the previous theory.

2. The predominance of the present scheme can also be shown from the viewpoint of the total energy. If the correlation function is chosen to be unit, then the present theory is reduced to the previous one exactly. It has been already 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 searching region is substantially equivalent to the set of PDs which are calculated by varying both correlation function and spin orbitals in Eq. (20). Therefore, the total energy of the present scheme is necessarily more sound than the previous one\[10\], and needless to say, than that of the Hartree-Fock approximation.

3. In addition to the above merits, the present scheme has the feature that deserves special emphasis. Due to the fact that the PD functional theory is still a developing field, there hardly exist the computational approaches so far. Our previous work is perhaps the first paper to propose a computational approach that incorporates both of problems related to PD functional theory\[10, 11\]. The present scheme is also a computational approach. The resultant simultaneous equations are quite tractable, as well as the previous one\[10, 11\]. Also from such a viewpoint, the present scheme seems to be valuable.

Thus, the resultant simultaneous equations (18) and (19) yield the PD which is definitely closer to the ground-state PD than the previous theory\[10\]. 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 prospect 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 potentiality to improve the approximation systematically.
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