A pair density functional theory utilizing the correlated wave function

M Higuchi
Department of Physics, Faculty of Science, Shinshu University, Matsumoto 390-8621, Japan
E-mail: higuchi@shinshu-u.ac.jp

K Higuchi
Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8527, Japan
E-mail: khiguchi@hiroshima-u.ac.jp

Abstract. We propose a practical scheme for calculating the ground-state pair density (PD) by utilizing the correlated wave function. As the correlated wave function, we adopt a linear combination of the single Slater determinants that are constructed from the solutions of the initial scheme[Higuchi M and Higuchi K 2007 Physica B 387, 117]. The single-particle equation is derived by performing the variational principle within the set of PDs that are constructed from such correlated wave functions. Since the search region of the PD is substantially extended as compared with the initial scheme, it is expected that the present scheme can cover more correlation effects. The single-particle equation is practical, and may be easily applied to actual calculations.

1. Introduction
The pair density (PD) functional theory has gotten a lot of attention recently, because it provides a possible way to go beyond the density functional theory. After the PD functional theory was proposed by Ziesche[1,2], a lot of works have been done so far[3-37]. However, almost all such works have been purely formal, and practical schemes for calculating the ground-state PD have been hardly reported so far. The lack of practical schemes in the PD functional theory is mainly due to the $N$-representability problem of the PD. Namely, if we employ the variational principle with respect to the PD, the search region of PDs is restricted within the set of $N$-representable PDs. Unfortunately, the necessary and sufficient conditions for $N$-representable PDs have not yet been obtained in a practical form although many attempts have been done so as to obtain them[21-37].

Recently, we have proposed a practical scheme for calculating the ground-state PD[16,17] by utilizing the extended constrained-search theory[38-41]. In this scheme, the search region of PDs is restricted in the set of PDs that are constructed from the single Slater determinants (SSDs). Namely, the best solution is searched within the set of restricted but definitely $N$-representable PDs. It can be characterized as the initial theory of the PD functional theory, because this scheme just corresponds to the Hartree-Fock approximation of the wave function theory and because this scheme provides a practical approach to calculate the ground-state PD[16,17,19]. Very recently, we have performed
actual calculations on the basis of this initial scheme, and illustrated that about 20% of the correlation energy is reproduced by this scheme[19].

Similarly to the Hartree-Fock approximation that gives a good starting point for more accurate wave function theory, various kinds of approaches to calculate the ground-state PD may be possible on the basis of the initial scheme. As the first step toward developing more accurate PD functional theory, we attempt to extend the search region of the ground-state PD in two ways, i.e., (a) by using the correlated wave function such as the Jastrow wave function[18], and (b) by means of the solutions of the initial scheme as basis functions of the variational method.

In this paper, we shall focus on the later attempt. This attempt is analogous to the configuration interaction method of the wave function theory, because the variational principle with respect to the PD is performed within the set of PDs that are given by a linear combination of SSD-PDs. The solutions of the initial scheme are utilized as the constituent orbitals of SSDs. As mentioned in the following section, the search region of PDs remains within the set of \( N \)-representable PDs. Due to the extension of the search region, we expect that the present scheme may cover more correlation effects than the initial scheme and may therefore be applicable to the strongly-correlated electron systems.

\section{2. An attempt beyond the initial PD functional theory}

With reference to the configuration interaction method in the wave function theory, we shall start with expanding the antisymmetric wave function with respect to SSDs:

\[
\Psi(x_1,x_2,\cdots,x_N) = \sum_i C_i \Phi_{\text{SSD},i}(x_1,x_2,\cdots,x_N),
\]

where \( \Phi_{\text{SSD},i}(x_1,x_2,\cdots,x_N) \) denote the SSDs calculated from the initial scheme[16,17,19]. In this paper, we consider only the case where the SSDs are different from each other in three or more constituent orbitals. Using the cofactor expansion of the SSD, it can be easily shown that an \( N \)-representable PD is expressed as the linear combination of the SSD-PDs. We have

\[
\gamma^{(2)}(rr';rr') = \sum_i |C_i|^2 \gamma^{(2)}_{\text{SSD},i}(rr';rr'),
\]

with

\[
\gamma^{(2)}_{\text{SSD},i}(rr';rr') = \frac{1}{2} \sum_{\alpha=1}^{N} \sum_{\beta=1}^{N} \left\{ \phi_\alpha^*(r) \phi_\beta^*(r') \left( \phi_\alpha(r) \phi_\beta(r') - \phi_\alpha^*(r) \phi_\beta^*(r') \phi_\alpha(r) \phi_\beta(r') \right) \right\},
\]

where \( \{ \phi_\alpha(r), \alpha = 1, 2, \cdots, N \} \) are the constituent orbitals of the SSD, which are normalized and orthogonal to each other.

We shall derive the effective single-particle equation that reproduces the ground-state PD. The total energy functional of the PD functional theory is given by [16,17,19]

\[
E[\gamma^{(2)}] = \text{Min} \left\{ \Psi | \hat{T} + \hat{W} | \Psi \right\} + \frac{2}{N-1} \int \gamma^{(2)}(rr';rr') v_{\text{ext}}(r) dr dr',
\]

where \( \hat{T} \) and \( \hat{W} \) are operators of the kinetic energy and electron-electron interaction, respectively, and where \( v_{\text{ext}}(r) \) denotes the external potential. The ground-state PD can be obtained by taking the minimization of the total energy functional with respect to the \( N \)-representable PDs [16,17,19]. This
problem corresponds to the variational problem of Eq. (4) with constraint that the PD should be \(N\)-representable. The constraint is simply written as

\[
\sum_i |C_i|^2 = 1. \tag{5}
\]

Here note that the PD that holds Eq. (5) is necessarily \(N\)-represetable even if the expansion is truncated at some finite term. This is a strong merit of the present scheme because the actual calculations inevitably employ the finite terms of Eq. (2) due to the computational resources.

Thus, using the Lagrange multiplier method, the resultant single-particle equation is given by

\[
\mu = \frac{4}{3} K \int \sum_i |C_i|^2 \gamma_{SSD,i}(rr'; rr') \, \frac{1}{|r-r'|} \, drdr' + \epsilon^2 \int \gamma_{SSD,i}(rr'; rr') \, v_{ext}(r) + v_{ext}(r') \, drdr',
\]

where \(\mu\) is the Lagrange multiplier. In the derivation of Eq. (5), we adopt the following approximate form as the kinetic energy functional:

\[
T[\gamma^{(2)}] = K \int \gamma^{(2)}(rr'; rr') \, drdr', \tag{7}
\]

where \(K\) is the constant factor[5,18]. This approximation is generally obtained with the aid of the scaling properties of the kinetic energy functional[5,18].

The next step is to check the performance by actual calculations. In the actual calculation, we first have to perform the initial scheme so as to get the SSD-PDs. Substituting these SSD-PDs into Eq. (6), we will find the self-consistent solution of the coefficients \(\{C_i\}\). The Lagrange multiplier \(\mu\) just corresponds to the total energy, so that we will solve the above equation to satisfy that the right-hand side of Eq. (6) is constant for any \(i\). This procedure may be performed without difficulty.

3. Concluding remarks

We have proposed a practical scheme for calculating the ground-state PD. In the present scheme, the variational principle with respect to the PD is performed within the set of PDs that are given by a linear combination of SSD-PDs. The search region is substantially extended in comparison with that of the initial scheme[16,17,19]. The merit of the present scheme is that the search region definitely remains within the set of \(N\)-representable PDs even though a linear combination of a small number of SSDs is adopted in Eq. (2). Therefore, the present scheme seems to cover more correlation effects than the initial scheme[16,17,19]. In addition, it is advantageous that the single-particle equation has a practical form. We have presented the computational procedure to solve the single-particle equation. Thus, the present scheme has the possibility to be an effective ab initio theory for the strongly-correlated electron systems.

Acknowledgments
This work was partially supported by Grant-in-Aid for Scientific Research (No. 19540399) and for Scientific Research in Priority Areas (No. 17064006) of The Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References

[1] Ziesche P 1994 Phys. Lett. A 195 213
[2] Ziesche P 1996 Int. J. Quantum Chem. 60 1361
[3] Gonis A, Schulthess T C, Ek J van and Turchi P E A 1996 Phys. Rev. Lett. 77 2981
[4] Gonis A, Schulthess T C, Turchi P E A and Ek J van 1997 Phys. Rev. B 56 9335
[5] Levy M and Ziesche P 2001 J. Chem. Phys. 115 9110
[6] Nagy Á 2002 Phys. Rev. A 66 022505
[7] Nagy Á and Amovilli C 2004 J. Chem. Phys. 121 6640
[8] Furche F 2004 Phys. Rev. A 70 022514
[9] Hetényi B, Brualla L and Fantoni S 2004 Phys. Rev. Lett. 93 170202
[10] Percus J K 2005 J. Chem. Phys. 122 234103
[11] Ayers P W 2005 J. Math. Phys. 46 062107
[12] Ayers P W and Levy M 2005 J. Chem. Sci. 117 507
[13] Nagy Á 2006 Int. J. Quantum Chem. 106 1043
[14] Ayers P W, Golden S and Levy M 2006 J. Chem. Phys. 124 054101
[15] Gori-Giorgi P and Savin A 2006 Philosophical Magazine 86 2643
[16] Higuchi M and Higuchi K 2007 Physica B 387, 117
[17] Higuchi M and Higuchi K 2007 J. Magn. Magn. Mater. 310, 990
[18] Higuchi M and Higuchi K 2007 Phys. Rev. A 75 042510
[19] Higuchi K and Higuchi M 2008 submitted to Phys. Rev. B
[20] Hetényi B and Hauser A W 2008 Phys. Rev. B 77 155110
[21] Coleman A J 1963 Rev. Mod. Phys. 35 668
[22] Coleman A J 1981 The Force Concept in Chemistry ed Deb B M (New York: Van Nostrand Reinhold) p 418
[23] Coleman A J and Yukalov V I 2000 Reduced Density Matrices: Coulson’s Challenge (Berlin: Springer-Verlag)
[24] Cioslowski J (ed) 2000 Many-electron Densities and Reduced Density Matrices (New York: Kluwer Academic/Plenum Publishers)
[25] Gidopoulos N I and Wilson S (eds) 2003 The fundamentals of electron density, density matrix and density functional theory in atoms, molecules and the solid states (New York: Kluwer Academic Press)
[26] Davidson E R 1995 Chem. Phys. Lett. 246 209
[27] Samvelyan S Kh 1997 Int. J. Quantum Chem. 65 127
[28] Pistol M -E 2004 Chem. Phys. Lett. 400 548
[29] Ayers P W and Levy M 2005 Chem. Phys. Lett. 415 211
[30] Pistol M -E 2006 Chem. Phys. Lett. 417 521
[31] Pistol M -E 2006 Chem. Phys. Lett. 422 363
[32] Ayers P W and Davidson E R 2006 Int. J. Quantum Chem. 106 1487
[33] Ayers P W 2006 Phys. Rev. A 74 042502
[34] Pistol M -E 2006 Chem. Phys. Lett. 431 216
[35] Pistol M -E 2007 Chem. Phys. Lett. 449 208
[36] Ayers P W and Davidson E R 2007 Adv. Chem. Phys. 134 443
[37] Ayers P W and Liu S 2007 Phys. Rev. A 75 022514
[38] Higuchi M and Higuchi K 2004 Phys. Rev. B 69 035113
[39] Higuchi K and Higuchi M 2004 Phys. Rev. B 69 165118
[40] Higuchi K and Higuchi M 2005 Phys. Rev. B 71 035116
[41] Higuchi M and Higuchi K 2008 submitted to Phys. Rev. B