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# Extension of the search region of pair densities by means of the scaling of the electron coordinates

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**Abstract.** We present a scheme for correcting the pair density (PD) to get it close to the ground state one. The search region of PDs is efficiently extended by adding the uniformly-scaled PDs to its elements. The key point is that the search region of PDs is kept within the set of  $N$ -representable PDs. The validity of this scheme is confirmed by numerical calculations of neutral neon atom. It is shown that the root-mean-square error of the electron-electron interaction and external potential energies, which can be a benchmark for the error of the PD, is reduced to about two-third without additional heavy calculations.

## 1. Introduction

Since the diagonal element of the second-order reduced density matrix, which is so-called the pair density (PD), has more information on the electron correlation than the electron density, it is expected that the PD functional theory will be a potential scheme beyond the conventional density functional theory [1–28]. Recently, we have developed the PD functional theories, on the basis of which actual calculations are feasible [19, 20, 25, 26, 28].

One of the difficulties in developing the PD functional theory is how to settle the variational search region of PDs within the set of  $N$ -representable PDs. Although we have to search the ground state PD within the set of the  $N$ -representable PDs (2nd Hohenberg-Kohn theorem of the PD functional theory), necessary and sufficient conditions for the  $N$ -representability of the PD have not yet been known in a practical form. We have recently attempted to utilize as the search region of PDs the set of PDs that come from some kind of antisymmetric wave functions [19, 20, 25, 26, 28]. In Ref. [28], we have extended the search region by constructing the PD from a linear combination of the Slater determinants (SDs). Although this extension method of the search region is a reliable and commonly-used one, it was also pointed out that a large number of SDs is needed for describing the electron correlation sufficiently [28]. More specifically, the reduction rate of errors of the PD is slow to the increasing the number of basis SDs. It has been eagerly anticipated an efficient scheme for extending the search region of PDs with keeping the  $N$ -representability.

In this paper, we propose an extension method for the search region of PDs. The search region is efficiently extended by adding a set of PDs, which are uniformly scaled with respect to the electron coordinates, to the elements of the search region. It is successfully confirmed that errors of the PD are remarkably reduced by about 30% without any heavy calculations.

Organization of this paper is as follows. In Sec. 2, we shall explain a new scheme for extending the search region of PDs. Numerical calculations are performed to check the validity of this scheme in Sec. 3. Some concluding remarks are given in Sec. 4.

## 2. Extension of the search region of PDs by means of the scaling technique

In this section, we shall explain a method to extend the search region of PDs by means of the scaling technique. First, we shall mention the scaling technique, and then present how to use the scaling technique in extending the search region of PDs.

Let us consider the scaling of electron coordinates ( $\mathbf{r}_i$ ) such that  $\mathbf{r}_i \rightarrow \lambda^{-1}\mathbf{r}_i$ , where  $\lambda$  is assumed to be positive. By the scaling of electron coordinates, the wave function  $\Psi(\mathbf{r}_1, \dots, \mathbf{r}_N)$  is transformed into

$$\Psi_\lambda(\mathbf{r}_1, \dots, \mathbf{r}_N) = \lambda^{3N/2}\Psi(\lambda\mathbf{r}_1, \dots, \lambda\mathbf{r}_N), \quad (1)$$

where  $\lambda^{3N/2}$  is a normalizing constant. The PD that is calculated from  $\Psi_\lambda$  is referred to as the scaled PD, and is given by

$$\gamma_\lambda^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \lambda^6\gamma^{(2)}(\lambda\mathbf{r}\lambda\mathbf{r}'; \lambda\mathbf{r}\lambda\mathbf{r}'), \quad (2)$$

where  $\gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$  is the PD that is calculated from  $\Psi$ . It is shown that the kinetic energy functional of the PD functional theory, which is denoted by  $T[\gamma^{(2)}]$ , satisfies the relation  $T[\gamma_\lambda^{(2)}] = \lambda^2T[\gamma^{(2)}]$  [6, 19, 25, 28]. This relation is so-called the scaling property of  $T[\gamma^{(2)}]$ , and is used as the restrictive condition in developing approximate forms of  $T[\gamma^{(2)}]$  [6, 19, 25, 28]. It can be also shown that the scaling properties of the electron-electron interaction energy  $W[\gamma^{(2)}]$  and the external potential energy  $V[\gamma^{(2)}]$  are given by  $W[\gamma_\lambda^{(2)}] = \lambda W[\gamma^{(2)}]$ , and  $V[\gamma_\lambda^{(2)}] = \lambda V[\gamma^{(2)}]$ , respectively. Here, we suppose for simplicity that the external potential energy is that of the isolated atomic system.

Next, we shall explain a method to extend the search region of PDs. Due to the variational principle with respect to the PD, the total energy functional  $E[\gamma^{(2)}] (= T[\gamma^{(2)}] + W[\gamma^{(2)}] + V[\gamma^{(2)}])$  takes its minimum at the correct ground-state PD if the minimum is searched within the set of all  $N$ -representable PDs ( $C_{\text{all}}$ ). However, as mentioned in Sec. 1, necessary and sufficient conditions for the  $N$ -representability of the PD have not yet been known in a practical form. We have recently proposed the methods to avoid this difficulty by using the subset of  $C_{\text{all}}$  as the search region of PDs [19, 25, 26, 28]. In previous works, the variationally-best PD  $\tilde{\gamma}_0^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$  is searched within the subset ( $C_1$ ) with the aid of the variational principle with respect to the PD [19, 25, 26, 28].

In the present method, the search region of PDs is extended by adding to  $C_1$  the set of scaled PDs that are given by  $\tilde{\gamma}_{0,\lambda}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \lambda^6\tilde{\gamma}_0^{(2)}(\lambda\mathbf{r}\lambda\mathbf{r}'; \lambda\mathbf{r}\lambda\mathbf{r}')$ . If we denote the set of scaled PDs as  $C_2$ , the new search region is expressed as  $C_1 \cup C_2$ . Note that all elements of PDs in the set  $C_1 \cup C_2$  are  $N$ -representable. Next, the variationally-best PD is searched within  $C_1 \cup C_2$ . If  $E[\tilde{\gamma}_{0,\lambda}^{(2)}]$  takes its minimum at  $\lambda = \Lambda$ , then we have  $dE[\tilde{\gamma}_{0,\lambda}^{(2)}]/d\lambda|_{\lambda=\Lambda} = 0$ . Using the scaling properties of  $T[\gamma^{(2)}]$ ,  $W[\gamma^{(2)}]$  and  $V[\gamma^{(2)}]$ , this condition for the minimum leads to

$$\Lambda = -\frac{W[\tilde{\gamma}_0^{(2)}] + V[\tilde{\gamma}_0^{(2)}]}{2T[\tilde{\gamma}_0^{(2)}]}. \quad (3)$$

From Eq. (3), we can determine the value of  $\Lambda$ . The scaled PD  $\tilde{\gamma}_{0,\Lambda}^{(2)}$  with  $\Lambda$  thus determined is the variationally-best one within the set  $C_1 \cup C_2$ . Of course,  $\tilde{\gamma}_{0,\Lambda}^{(2)}$  remains  $N$ -representable. The kinetic energy, electron-electron interaction energy and the external potential energy for the PD  $\tilde{\gamma}_{0,\Lambda}^{(2)}$  can be easily calculated from their scaling properties, respectively. Furthermore, it is found from Eq. (3) that the virial relation exactly holds for  $\tilde{\gamma}_{0,\Lambda}^{(2)}$ . It should be noted that the present method needs no heavy calculation tasks for obtaining  $\tilde{\gamma}_{0,\Lambda}^{(2)}$  and related quantities.

### 3. Test calculations

In order to check to the validity of the present method, actual calculations are performed for Ne atom. Concerning the approximate form of  $T[\gamma^{(2)}]$ , we employ the following approximate form [28],

$$T[\gamma^{(2)}] = \int \int \left\{ K \left( \frac{1}{r^2} + \frac{1}{r'^2} \right) + \frac{K'}{rr'} \right\} \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r d^3r' \quad , \quad (4)$$

where  $K$  and  $K'$  are arbitrary constants. This approximate functional has been developed by imposing restrictive conditions for  $T[\gamma^{(2)}]$  on it, and shows good abilities in the previous work [28]. Arbitrary constants  $K$  and  $K'$  are determined by requiring the approximate functional to have two desirable features. One is that the approximate functional yields the Hartree-Fock kinetic energy for the Hartree-Fock PD. The other is that the root-mean-square error (RMSE) of the external potential and electron-electron interaction energies is minimized with respect to  $K$  and  $K'$ .

In the test calculations, we employ as  $C_1$  the set of PDs that are constructed by the linear combinations of 2,861 Slater determinants (SDs) [28]. The variationally-best PD within the set  $C_1$ , which corresponds to  $\tilde{\gamma}_0^{(2)}$ , is first calculated by means of the computational PD functional scheme [28]. Next, according to the procedure mentioned in the previous section,  $\tilde{\gamma}_{0,\Lambda}^{(2)}$ ,  $T[\gamma_{0,\Lambda}^{(2)}]$ ,  $W[\gamma_{0,\Lambda}^{(2)}]$  and  $V[\gamma_{0,\Lambda}^{(2)}]$  are calculated. For comparison, we also calculate the variationally-best PD within the search region that is extended with increasing the number of basis SDs (NSD) from 2,861 to 12,275. Hereafter, this search region is denoted as  $C_1'$ .

Table 1 shows the calculation results. In Tab. 1,  $\Delta W$ ,  $\Delta V$  and  $\Delta T$  denote errors of the electron-electron interaction energy, external potential energy and kinetic energy, respectively, and  $R_v$  stands for the virial ratio. From Tab. 1, both  $\Delta W$  and  $\Delta V$  for the present method (search region  $C_1 \cup C_2$ ) are much improved as compared with those for  $C_1$ . The resultant RMSE for  $C_1 \cup C_2$  is reduced to 61% from that for  $C_1$ . Therefore, we may say that the resultant PD of the present method,  $\tilde{\gamma}_{0,\Lambda}^{(2)}$ , approaches to the correct ground state PD. On the other hand,  $\Delta W$ ,  $\Delta V$ , RMSE for  $C_1'$  are only slightly smaller than those for  $C_1$ . Thus, the search region of PDs is extended more efficiently by adding  $C_2$  to  $C_1$  than by increasing the NSD.

It is also found from Tab. 1 that  $\Delta T$  is reduced more effectively by the present method than by increasing the NSD. The errors of the kinetic energy originate from both the errors of the approximate form and the resultant PD. As mentioned above, the resultant PD seems to be much improved by the present method. Therefore, we can say that the approximate form exhibits appropriate behavior.

Finally, we shall give a comment on the calculation result of  $R_v$ . As mentioned in the previous section, the virial relation exactly holds for  $\tilde{\gamma}_{0,\Lambda}^{(2)}$ . This is one of the features of the present method. This feature is confirmed in the actual calculations, i.e.,  $R_v$  takes the correct value of -2.0 for the present method.

**Table 1.** Results of test calculations

search region	$\Delta W(\%)$	$\Delta V(\%)$	RMSE(%)	$\Delta T(\%)$	$R_v$
$C_1$	0.103	-0.364	0.268	-0.637	-2.004
$C'_1$	0.102	-0.358	0.263	-0.642	-2.004
$C_1 \cup C_2$	0.039	-0.228	0.164	-0.284	-2.000

#### 4. Concluding remarks

In this paper, we present a correction scheme for the ground-state PD. Scaling the PD with respect to the electron coordinates, the PD is varied with it kept  $N$ -representable. In order to compare the present scheme with the usual one [28], we use the same approximate functional of the kinetic energy that was used in Ref. [28]. Numerical calculations for Ne atom show that the search region of PDs is extended more efficiently by the present scheme than by the usual one [28]. The idea of the present scheme, which utilizes the scaling technique so as to vary the variational function, would have extensive applications such as the wave function theory and other types of the density functional schemes.

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