A correction method for the pair density to get close to the ground state one

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We present a correction method for the pair density (PD) to get close to the ground state one. The PD is corrected to be a variationally-best PD within the search region that is extended by adding the uniformly-scaled PDs to its elements. The corrected PD is kept N-representable and satisfies the virial relation rigorously. The validity of the present method is confirmed by numerical calculations of neon atom. It is shown that the root-mean-square error of the electron-electron interaction and external potential energies, which is a good benchmark for the error of the PD, is reduced by 69.7% without additional heavy calculations.

The electron correlation is one of main topics in the fields of the atomic, molecular and condensed matter physics. The physical quantity that directly expresses the electron correlation is the diagonal element of the second-order reduced density matrix, which is so-called the pair density (PD). The PD gives not only the correlation beyond the conventional density functional theory (PDFT)\cite{1–3, 20–29}. In this letter, we present a correction method for the PD to get close to the ground state one, in which the search region of PDs is substantially extended. This method can become a powerful tool to overcome the well-known problems of the PDFT.

There exist two kinds of well-known problems in developing the PDFT. One is to have to develop the approximate form of the kinetic energy functional since the kinetic energy cannot be expressed by the PD alone\cite{1–3, 20–29, 30–33}. Some approximation is needed for the kinetic energy cannot be expressed by the PD alone\cite{1–3, 20–29}. Therefore, the PD functional theory (PDFT)\cite{4–33} is one of the promising first-principle methods for describing the electron correlation beyond the conventional density functional theory\cite{34, 35}. In this letter, we present a correction method for the PD to get close to the ground state one, in which the search region of PDs is substantially extended. This method can become a powerful tool to overcome the well-known problems of the PDFT.

Concerning the first problem we propose an approximate functional of the kinetic energy along the strategy shown in the previous paper\cite{19}. Namely, an approximate functional is developed by imposing two kinds of sum rules for the kinetic energy functional as the restrictive conditions. Although the previous approximate functionals have been developed by imposing excessively the restrictive conditions on them\cite{19}, the present one is devised with removing such excessive restrictive conditions\cite{19, 36}. We have

\[ T[\gamma^{(2)}] = \int \left\{ \frac{K}{\gamma^2} + K' \frac{\cos \theta}{\gamma^2} \ln \left( \frac{r}{\gamma} \right) \right\} \gamma^{(2)}(rr'; rr') \, drr', \]

where \( \gamma^{(2)}(rr'; rr') \) denotes the PD, and where \( K \) and \( K' \) are arbitrary constants that are determined later. Equation (1) satisfies the scaling property of the kinetic energy functional and is consistent with the HK theorem of the PDFT\cite{19, 36}. The former fact will be significant later in discussing a correction method.

Concerning the second problem, we have recently attempted to extend the variational search region of PDs\cite{17, 19} beyond that of the effective initial theory\cite{16, 18}. However, it has been eagerly anticipated that such a search region is further extended with keeping the N-representability of the PD. In this letter, we shall extend the search region by adding another set of PDs to the elements of the search region. This is precisely our correction method, and is a main subject of this letter. Let us show this method in the following three steps (i), (ii) and (iii).

(i) First of all, we shall show that the kinetic energy functional which is consistent with the scaling property satisfies the virial relation exactly. Here suppose that the search region of PDs fully covers a set of the N-representable PDs. Applying the scalings of the electron coordinates, \( \gamma^{(2)}(rr'; rr') \) is transformed into

\[ \gamma^{(2)}(rr'; rr') = \lambda^2 \gamma^{(2)}(\lambda r \lambda r'; \lambda r \lambda r'), \]

where \( \lambda \) is the scaling parameter, \( \gamma^{(2)}(rr'; rr') \) is the PD scaled from \( \gamma^{(2)}(rr'; rr') \), which is called the scaled PD. The kinetic energy functional that is consistent with the scaling property satisfies the following relation\cite{8, 16, 19}:

\[ T[\gamma^{(2)}] = \lambda^2 T[\gamma^{(2)}]. \]
Similarly, the electron-electron interaction and external potential energies to the scaled PD are, respectively, given by

\[
W[\tilde{\gamma}^{(2)}] = \lambda W[\gamma^{(2)}],
\]
and

\[
V[\tilde{\gamma}^{(2)}] = \frac{2}{N-1} \int v_{\text{ext}}(\tilde{r}) \gamma^{(2)}(\tilde{r}'; \tilde{r}') d\tilde{r}' d\tilde{r},
\]

where \(v_{\text{ext}}(r)\) denotes the external potential and where \(N\) is the number of electrons. Due to the 2nd HK theorem of the PDFT, the total energy functional \(E[\gamma^{(2)}] = T[\gamma^{(2)}] + W[\gamma^{(2)}] + V[\gamma^{(2)}]\) is minimum at \(\gamma^{(2)}\) that corresponds to the variationally-best PD among all of the \(N\)-representable PDs. Using the scaled PD, the theorem can be written as \(dE[\gamma^{(2)}_0, \Lambda]/d\lambda|_{\lambda=1} = 0\). Here \(\gamma^{(2)}_0\) is the PD scaled from \(\gamma^{(2)}\), and is defined similarly to Eq. (2). Substituting Eqs. (3), (4) and (5) into this theorem, we have

\[
2T[\tilde{\gamma}^{(2)}_0] + W[\tilde{\gamma}^{(2)}_0] = \int \frac{\|\mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r})\|}{N-1} \gamma^{(2)}_0(\mathbf{r}'; \mathbf{r}') d\mathbf{r}' d\mathbf{r}.
\]

Equation (6) is the virial relation of the PDFT. It should be noted that even though the kinetic energy functional that satisfies Eq. (3) is not an exact but an approximate form, Eq. (6) exactly holds if the search region fully covers the set of the \(N\)-representable PDs.

(ii) Next, we shall consider the case where the search region not fully but partially covers a set of the \(N\)-representable PDs. Suppose that such a partial search region is denoted as \(C_1\) (See, Fig. 1), and that the total energy functional is minimum at \(\gamma^{(2)}_0\) that corresponds to the variationally-best PD within the set \(C_1\). Due to the incomplete cover of \(N\)-representable PDs by the set \(C_1\), it could be that not all of the scaled PDs \(\tilde{\gamma}^{(2)}_{0,\Lambda}\) are included in the set \(C_1\). We denote the set of \(\tilde{\gamma}^{(2)}_{0,\Lambda}\) as \(C_2\) (Fig. 1).

In this case, the total energy functional \(E[\tilde{\gamma}^{(2)}_{0,\Lambda}]\) does not always take the minimum at \(\lambda = 1\). Namely, we have \(dE[\tilde{\gamma}^{(2)}_{0,\Lambda}] / d\lambda|_{\lambda=1} \neq 0\). Like the derivation of Eq. (6), this inequality leads to the relation such that the left-hand side of Eq. (6) is not equal to the right-hand side. Thus, if the search region does not fully cover the set of the \(N\)-representable PDs, the virial relation does not hold even though the kinetic energy functional satisfies Eq. (3). This fact can be used as a criterion of whether the search region fully covers the set of the \(N\)-representable PDs or not. Here let us define the virial ratio which indicates to what extent the virial relation holds:

\[
R_v = \frac{W[\tilde{\gamma}^{(2)}_0] - \int \frac{\|\mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r})\|}{N-1} \tilde{\gamma}^{(2)}_0(\mathbf{r}'; \mathbf{r}') d\mathbf{r}' d\mathbf{r}}{T[\tilde{\gamma}^{(2)}_0].}
\]

Using this ratio, the above-mentioned criterion can be restated as follows; the deviation of \(R_v\) from the value -2.0 means the insufficiency of the search region of PDs if the kinetic energy functional satisfies Eq. (3).

(iii) When \(R_v\) deviates from -2.0, a correction method that is related to the extension of the search region is desired. The key point of the present correction method is the extension of the search region by adding the scaled PDs to the search region. Figure 1 truly shows the relation between the original search region \(C_1\) and newly-added search region \(C_2\). Both sets \(C_1\) and \(C_2\) are subsets of the set of the \(N\)-representable PDs. The above-mentioned inequality \(dE[\tilde{\gamma}^{(2)}_{0,\Lambda}] / d\lambda|_{\lambda=1} \neq 0\) means that the set \(C_2\) could possibly include the PD that takes a total energy lower than what the best PD within the set \(C_1\), i.e., \(\tilde{\gamma}^{(2)}_0\), takes. Such a PD exists in \(C_2 \cap C_1\) and is denoted as \(\tilde{\gamma}^{(2)}_{0,\Lambda}\), where \(C_1\) is the complementary set of \(C_1\) (Fig. 1). Then, the inequality \(dE[\tilde{\gamma}^{(2)}_{0,\Lambda}] / d\lambda|_{\lambda=1} = 0\) is rewritten as \(dE[\tilde{\gamma}^{(2)}_{0,\Lambda}] / d\lambda|_{\lambda=\Lambda} = 0\). Substituting Eqs. (3), (4) and (5) into this equation, we obtain

\[
2\Lambda T[\tilde{\gamma}^{(2)}_{0,\Lambda}] + W[\tilde{\gamma}^{(2)}_{0,\Lambda}] = \int \frac{\|\mathbf{r} \cdot \nabla v_{\text{ext}}(\mathbf{r})\|}{\Lambda^2(N-1)} \tilde{\gamma}^{(2)}_{0,\Lambda}(\mathbf{r}'; \mathbf{r}') d\mathbf{r}' d\mathbf{r}.
\]

If we consider the isolated atomic system, Eq. (8) is easily rewritten as

\[
2\Lambda T[\tilde{\gamma}^{(2)}_{0,\Lambda}] + W[\tilde{\gamma}^{(2)}_{0,\Lambda}] = -V[\tilde{\gamma}^{(2)}_{0,\Lambda}].
\]

From Eq. (8) or (9), we can determine the value of \(\Lambda\). The scaled PD \(\tilde{\gamma}^{(2)}_{0,\Lambda}\) with \(\Lambda\) thus determined is the variationally-best one within the union of two sets, i.e., \(C_1 \cup C_2\). That is to say, a correction of the ground state PD from \(\tilde{\gamma}^{(2)}_0\) to \(\tilde{\gamma}^{(2)}_{0,\Lambda}\) is accomplished by extending the search region from \(C_1\) to \(C_1 \cup C_2\). It is obvious that the corrected PD \(\tilde{\gamma}^{(2)}_{0,\Lambda}\) remains \(N\)-representable. Furthermore, it is easily confirmed that the virial relation exactly holds for the corrected PD \(\tilde{\gamma}^{(2)}_{0,\Lambda}\).
increasing the number of basis SDs (NSD) from 2,861 to 12,275 in \( \Delta W \) and \( \Delta V \), respectively (reduction from case \( a \) to \( c \) for “\( \Delta W \)” and “\( \Delta V \)”, respectively, in Fig. 2). On the other hand, only 1.3% and 1.1% reductions are made via increasing the NSD from 2,861 to 12,275 in \( \Delta W \) and \( \Delta V \), respectively (reduction from case \( a \) to \( b \) for “\( \Delta W \)” and “\( \Delta V \)”, respectively). Also, as shown in Fig. 2, the RMSE is remarkably reduced by 69.7% (reduction from case \( a \) to \( c \)) and 66.3%, respectively. Thus, the reduction rate of the present method is much larger than that of the extension method with increasing the NSD. This leads to that the search region of PDs is more effectively extended by adding the uniformly-scaled PDs than by increasing the NSD. Furthermore, it should be noticed that the present method is feasible without additional heavy calculations.

(II) It is found in Fig. 2 that \( \Delta T \) is also reduced much more effectively by the present method than by increasing the NSD (80.9% and 1.2% reductions for the former and latter, respectively). In general, the accuracy of the kinetic energy is dependent on both the appropriateness of the approximate form of the functional and that of the resultant PD. Judging from the results of the RMSE, \( \Delta W \) and \( \Delta V \) (Fig. 2), the resultant PD seems to be improved to be close to the ground state one. Therefore, we can deduce that the approximate form itself, which is given by Eq. (1), would be also sound.

(III) It is found in Fig. 2 that the virial ratios \( R_v \) before the correction deviate from the correct value \( -2.0 \). Using the criterion on the search region, these deviations mean that not only the search region \( C_1 \) but also the electron-electron interaction energy, external potential energy, kinetic energy and virial ratio that are denoted by \( \Delta W \), \( \Delta V \), \( \Delta T \) and \( \Delta R_v \), respectively. The root-mean-square error (RMSE) of the electron-electron interaction and external potential energies is also calculated by \( \sqrt{\frac{(\Delta W)^2 + (\Delta V)^2}{2}} \). The RMSE is considered as a good benchmark for to what extent the resultant PD is close to the correct ground state PD. This is because accuracies of both the electron-electron interaction and external potential energies are dependent only on that of the PD.

The above-mentioned calculations are performed with changing the values of \( K \) and \( K' \) that appear in Eq. (1). These values are determined by requiring the approximate functional to have two desirable features. One is that the approximate functional reproduces the Hartree-Fock kinetic energy if the PD coincides with the Hartree-Fock PD. The other is that the RMSE of the electron-electron interaction and external potential energies is minimized with respect to parameters. This determination process is implemented in individual cases before and after the correction.

Calculation results are shown in Fig. 2. From this figure, we find the following points.

(I) It is found in Fig. 2 that the present method reduces \( \Delta W \) and \( \Delta V \) by 89.7% and 66.3%, respectively (reductions from case \( a \) to \( c \) for “\( \Delta W \)” and “\( \Delta V \)”, respectively, in Fig. 2). On the other hand, only 1.3% and 1.1% reductions are made via increasing the NSD from 2,861 to 12,275 in \( \Delta W \) and \( \Delta V \), respectively (reduction from case \( a \) to \( b \) for “\( \Delta W \)” and “\( \Delta V \)”, respectively). Also, as shown in Fig. 2, the RMSE is remarkably reduced by 69.7% (reduction from case \( a \) to \( c \)) and 66.3%, respectively. Thus, the reduction rate of the present method is much larger than that of the extension method with increasing the NSD. This leads to that the search region of PDs is more effectively extended by adding the uniformly-scaled PDs than by increasing the NSD. Furthermore, it should be noticed that the present method is feasible without additional heavy calculations.

(II) It is found in Fig. 2 that \( \Delta T \) is also reduced much more effectively by the present method than by increasing the NSD (80.9% and 1.2% reductions for the former and latter, respectively). In general, the accuracy of the kinetic energy is dependent on both the appropriateness of the approximate form of the functional and that of the resultant PD. Judging from the results of the RMSE, \( \Delta W \) and \( \Delta V \) (Fig. 2), the resultant PD seems to be improved to be close to the ground state one. Therefore, we can deduce that the approximate form itself, which is given by Eq. (1), would be also sound.

(III) It is found in Fig. 2 that the virial ratios \( R_v \) before the correction deviate from the correct value \( -2.0 \). Using the criterion on the search region, these deviations mean that not only the search region \( C_1 \) but also the
In constructing PDs, the search region is not extended effectively. On the other hand, it is to say, even though more than 12,000 SDs are used, the functional Eq. (1) is consistent with Eq. (3). That is to say, even though more than 12,000 SDs are used in constructing PDs, the search region is not extended effectively. We can therefore say that the PD is corrected rigorously equal to -2.0, as it should be. These tendencies seem to be consistent with those mentioned in the above (I) and (II).

Thus, the present method improves not only \( \Delta W \), \( \Delta V \) and RMSE but also \( \Delta T \) and \( \Delta R_v \) quite substantially and effectively. We can therefore say that the PD is corrected to be close to the ground-state one appropriately via the present method.

In conclusion, we summarize the features of the correction method proposed here. The most distinctive feature is that

1. the search region is extended by adding a set of the scaled PDs to elements of the search region.
2. the corrected PD is \( N \)-representable.
3. the corrected PD satisfies the virial relation exactly.
4. not only the RMSE but also the errors of the kinetic energy, electron-electron interaction energy and external potential energy are individually all reduced definitely.
5. the correction is enough effective even in the small size calculations.

This correction method provides an ingenious way to extend the search region of PDs efficiently. Due to the computational easiness of the correction, this method will be extensively applicable to larger systems such as molecules, clusters and solids.

Note that covers fully the set of the \( N \)-representable PDs.

FIG. 2: The calculation results of the \( \Delta W \), \( \Delta V \), RMSE, \( \Delta T \) and \( \Delta R_v \). In this figure, the search region \( C_1 \), \( C'_1 \) and \( C_1 \cup C_2 \) are simply denoted by the symbols "a", "b" and "c", respectively.