A Proposal of the Approximate Kinetic Energy Functional of the Pair Density Functional Theory

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We propose the approximate kinetic energy (KE) functional of the pair density (PD) functional theory on the basis of the coupling-constant expression that is recently derived [Phys. Rev. A **85** (2012) 062508]. The proposed KE functional, which is called the "correlated Gaussian model", consists of the modified version of the Thomas-Fermi (TF) model and correlation energy functional of the local density approximation. We check the validity of the correlated Gaussian model by means of numerical calculations for the Ne atom. It is shown that the correlated Gaussian model gives better results of not only the KE, Hartree energy, exchange-correlation (xc) energy, potential energy but also the xc-hole than the previously proposed correlated TF model [J. Phys.: Conference Series. **454** (2013) 012056].

KEYWORDS: Pair density, Pair density functional theory, exchange-correlation hole, Kinetic energy functional, Gaussian model

1. Introduction

The pair density (PD), which is the diagonal element of the 2nd-order reduced density matrix, has more information about the electron correlation than the electron density [1-3]. For example, we can calculate the spatial profile of the exchange-correlation (xc) hole as well as the xc energy from the PD. Therefore, the PD functional theory [4-37], which can reproduce the ground-state PD, has recently attracted much attention as a potential scheme that can describe the electron correlation of the strongly correlated electron system more appropriately than the conventional density functional theory (DFT) [38,39].

In order to develop the PD functional theory, there exist two kinds of problems. One is how to set the search region of PDs. Another problem is how the kinetic energy (KE) is expressed as a functional of the PD. These two problems should be solved simultaneously.

Concerning the first problem, there are a lot of works where the necessary and sufficient conditions for the N-representability of the PD are discussed [1-3, 24-33]. However, the necessary and sufficient conditions are not yet known in a practical form. In order to avoid the first problem, we have proposed several schemes [16-20, 22]. The key point of our schemes is how the search region of PDs is extended with keeping their N-representability [16-20, 22]. Most recently, we have developed the PD

functional theory utilizing the electron coordinates scaling [20, 22]. This method can substantially extend the search region of PDs without heavy calculation tasks, and is called the "scaling method" [20, 22]. This method is employed in this paper when we check the validity of the approximate KE functional (§3).

Concerning the second problem, there have been two strategies so far. One is to utilize the exact relations for the KE functional as restrictive conditions in devising the approximate form [21]. Several approximations have been developed along this strategy [16-22]. Another is to develop the approximate form by utilizing the coupling-constant expression that is a rigorous expression of the KE functional [21]. Also along this strategy, we have already proposed the approximate form of the KE functional which has the form such as the noninteracting KE minus the correlation energy [21]. In the previous work [23], we adopt the Thomas-Fermi (TF) functional and local density approximation (LDA) of the DFT as the noninteracting KE and correlation energy, respectively. This model is the first approximate functional that is derived from the coupling-constant expression, and is called the "correlated TF model" [23]. From actual calculations, it is shown that there is room for improvement in this initial model [23].

In this paper, in order to develop more appropriate KE functional, we take the latter strategy mentioned above. Specifically, the "correlated Gaussian model" is proposed by adopting as the noninteracting KE the Gaussian model that is the modified version of the TF model [40, 41]. We also check the validity of the correlated Gaussian model through numerical calculations for the Ne atom.

Organization of this paper is as follows. In §2, we give the explicit form of the correlated Gaussian model that is derived from the coupling-constant expression. In §3, we present calculation results and discuss the validity of the correlated Gaussian model. Finally, the concluding remarks are given in §4.

2. Approximate form of the KE functional

We shall denote the PD as $\gamma^{(2)}$. On the basis of the coupling-constant expression of the KE functional, we have already shown that the KE functional $T\left[\gamma^{(2)}\right]$ can be approximated by [21]

$$T\left[\gamma^{(2)}\right] \approx T_s\left[\gamma_{SD}^{(2)}\right] - \left\{ W\left[\gamma^{(2)}\right] - \left\langle \Phi\left[\gamma_{SD}^{(2)}\right] \middle| \hat{W} \middle| \Phi\left[\gamma_{SD}^{(2)}\right] \right\rangle_{\Omega} \right\}, \tag{1}$$

where $\gamma_{SD}^{(2)}$, $\Phi\left[\gamma_{SD}^{(2)}\right]$ and $T_s\left[\gamma_{SD}^{(2)}\right]$ denote the ground-state PD, wave function and KE of the noninteracting reference system [16,17], respectively, and where $W\left[\gamma^{(2)}\right]$ and $\hat{W}$ are the electron-electron interaction energy and its operator, respectively. It should be noted that $\gamma_{SD}^{(2)}$ is a functional of $\gamma^{(2)}$ [21]. In order to get the tractable approximate form of the KE, we adopt as $T_s\left[\gamma_{SD}^{(2)}\right]$ the Gaussian model $T_{Gauss}\left[\rho\right]$ [40, 41]. Here, ρ denotes the electron density. Concerning the second term of eq. (1), it may be approximated by the correlation energy functional of the DFT because the magnitude of $W\left[\gamma^{(2)}\right] - W\left[\gamma_{SD}^{(2)}\left[\gamma^{(2)}\right]\right]$ of eq. (1) is expected to be comparable to that of the correlation energy [21]. In this study, we adopt the LDA ($E_c^{LDA}\left[\rho\right]$) [42] as the correlation energy functional. Thus, we get the approximate form:

$$T_{cG}\left[\gamma^{(2)}\right] = T_{Gauss}\left[\rho\right] - E_c^{LDA}\left[\rho\right], \tag{2}$$

with

$$T_{Gauss}\left[\rho\right]=\frac{3\pi}{2^{2/3}}\int\rho(\boldsymbol{r})^{5/3}\mathrm{d}^3r \ , \tag{3}$$

and

$$\rho(\boldsymbol{r})=\frac{2}{N-1}\int\gamma^{(2)}(\boldsymbol{r}\boldsymbol{r}';\boldsymbol{r}\boldsymbol{r}')\mathrm{d}^3r' \ , \tag{4}$$

where N is the number of electrons. This approximation is called "correlated Gaussian model" hereafter. As compared with the correlated TF model [23], the first term of eq. (2) is replaced by the Gaussian KE in the present model.

3. Test Calculations

In order to test the correlated Gaussian model, the atomic structure of the neutral Ne is calculated by utilizing the scaling method [20, 22]. In the scaling method, we first determine the "Seed PD" that is defined as the variationally-best PD within the smaller size of the search region. In the test calculations, the set of PDs that are constructed from the multiple Slater determinants is used in determining the seed PD [19]. The details of the calculation procedure are given in the previous paper [23]. Totally, 1,342 Slater determinants are used in the present calculations.

We calculate the KE (T), electron-electron interaction energy (W), potential energy (V), virial ratio (R_v), Hartree energy (U), xc energy (E_{xc}) and total energy (E). The calculation results are summarized in Table I. For comparison, the calculation results that have been obtained by using the correlated TF functional [23] are also listed in Table I. Except for W, the correlated Gaussian model provides better results than the correlated TF model. It should be noticed from Table I that smaller error of W for the correlated TF model is due to the accidental cancelation of errors of U and E_{xc}. Such an accidental cancelation does not occur in the case of the correlated Gaussian model. Judging from the fact that both errors of U and E_{xc} are reduced by using the correlated Gaussian model instead of the correlated TF model, it is reasonably concluded that the resultant PD by the correlated Gaussian model is more close to the true grand-state PD than that by the correlated TF model.

In order to show further the superiority of the correlated Gaussian model to the correlated TF one, we also calculate the electron density and xc-hole. Figure 1 shows the electron density of the correlated Gaussian model together with those of the configuration interaction (CI) method [44] and the correlated TF model [23]. The first peak of the present profile gets close to the CI result while the second peak gets worse. The first peak contributes to V more significantly than the second one, because the first one is located near the nucleus than the second one, and because its magnitude is larger than that of the second one. Correspondingly, V is improved by using the correlated Gaussian model as shown in Table I. In addition, the Hartree energy U is improved in the correlated Gaussian model as shown in Table I. This can be understood in such a way that the electron density around the first peak would result in more contribution to the Hartree energy than that around the second one.

Table I. The KE (T), electron-electron interaction energy (W), potential energy (V), total energy (E), virial ratio (R_v), Hartree energy (U) and xc energy (E_{xc}) are shown together with their errors to the reference data.   Results of the correlated Gaussian model (correlated TF model) are shown in the first (second) row [23].   The reference data are also shown in the third row [43].

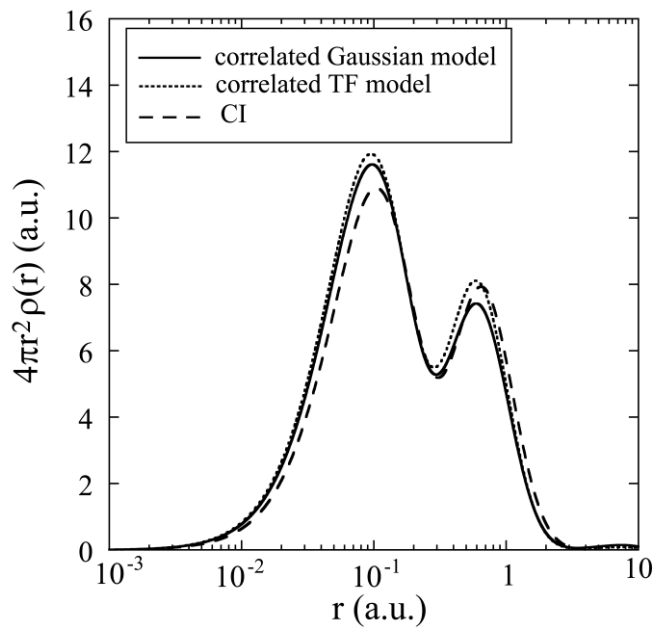|	T(ryd.)	W(ryd.)	V(ryd.)	E(ryd.)	R_v	U(ryd.)	E_{xc}(ryd.)
Correlated Gaussian	270.00	99.55	-640.59	-271.04	-2.0039	129.35	-29.81
	(4.70%)	(-6.48%)	(2.96%)	(5.11%)	(0.19%)	(-2.05%)	(-16.34%)
Correlated TF [23]	278.30	109.24	-667.03	-279.49	-2.0043	124.70	-15.46
	(7.92%)	(2.63%)	(7.21%)	(8.38%)	(0.21%)	(-5.57%)	(-39.67%)
Reference data [43]	257.87	106.44	-622.19	-257.87	-2.0000	132.06	-25.62

Fig. 1. Profiles of the electron density of the neutral Ne atom.

Figure 2 shows the xc-hole along the z axis for the Ne atom, together with the corresponding xc-holes calculated by the CI method and the correlated TF model. These profiles are calculated under the condition that the reference electron is placed at z = 0.2.   It is found from Fig. 2 that the xc-hole is much improved by using the correlated Gaussian model.   This result is consistent with the improvement in E_{xc} (Table I).   Therefore, we can say that the resultant PD by the correlated Gaussian model gets closer to the true ground-state PD than that by the correlated TF model.

Finally, we give a brief comment on the soundness of the correlated Gaussian model. As shown in Table I, the error of the KE of the correlated Gaussian is smaller than that of the correlated TF model. The error of the KE is caused by both the appropriateness of the approximate KE functional and the error of the PD. Therefore, with the above-mentioned improvement of the resultant PD in mind, this error reduction in the KE would mean the soundness of the correlated Gaussian model.
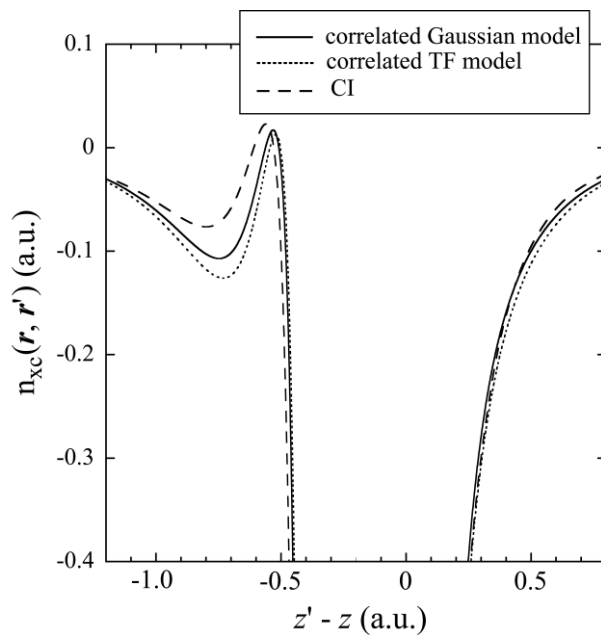

Fig. 2. Profiles of the xc-hole of the neutral Ne atom.

4. Conclusion

In order to develop the PD functional theory, we propose the correlated Gaussian model as the approximate KE functional. This approximate form is devised by using the coupling-constant expression of the KE functional. The correlated Gaussian model is regarded as the modified version of the correlated TF model that has been developed for the first time on the basis of the coupling-constant expression. It is found from numerical calculations that the correlated Gaussian model exhibits the better results than the correlated TF model. This means that the usage of the coupling-constant expression in developing the approximate KE functional would be one of the promising ways to get more accurate KE functional.

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