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2013 J. Phys.: Conf. Ser. 454 012056

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Checking the validity of the correlated Thomas-Fermi functional in the pair density functional theory

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Abstract. To check the validity of the recently proposed kinetic energy (KE) functional of the pair density (PD) functional theory, we perform the numerical calculation for the neutral Ne atom. This is the first computational trial for the PD functional theory which includes the KE functional that is approximately derived on the basis of the rigorous expression with the coupling-constant integration. In this work we adopt the correlated Thomas-Fermi functional as the approximate KE functional. Although it is shown that non-negligible errors exist in the resulting PD, the present results will be useful as reference data in cases of developing further the approximate KE functional.

1. Introduction

The pair density (PD) functional theory [1-33] is expected to be a promising theory to go beyond the conventional density functional theory (DFT) [34, 35]. In developing the PD functional theory, there exist two kinds of problems that need to be overcome [3-33]. One is how we devise to extend the search region of PDs within the set of N -representable PDs [3-22, 27-33]. The other is how we develop the approximate form of the kinetic energy (KE) functional [23-33].

Concerning the first problem, we have recently proposed a correction method for obtaining the variationally best ground-state PD [31]. It has been shown that the search region of PDs is substantially extended by adding the scaled PDs as elements of the search region [31].

To overcome the second problem, we can take two strategies in a similar way to the development of the exchange-correlation (xc) energy functional of the conventional DFT and its extensions [36-41]:

- (i) Rigorous relations and bounds that should be fulfilled by the KE functional are utilized as restrictive conditions on the approximate form.
- (ii) On the basis of the coupling-constant expression for the KE functional, the approximate form is developed.

Several types of approximate KE functionals have already been developed along the above strategy (i)[30]. Specifically, approximate KE functionals are developed by requiring them to satisfy the scaling property of the KE functional [5] and the Hohenberg-Kohn theorem of the PD functional theory [30]. We have furthermore begun numerical calculations to check their validities [30].

In this paper, we attempt the second strategy. We have recently derived the coupling-constant expression for the KE functional [32]. Since it is rigorous, this expression would be a good starting point for developing the approximate functional. Actually, using the perturbation theory, we have also proposed the approximate form on the basis of this expression [32]. The resultant form is written as the sum of the noninteracting KE functional and correlation energy functional [32]. In this paper, we adopt as such functionals the Thomas-Fermi (TF) functional and correlation energy functional of the local density approximation (LDA), respectively. Hereafter, this approximate form is called the



correlated TF functional. In this paper, we check the validity of the correlated TF functional by means of numerical calculations of the Ne atomic structure.

Organization of this paper is as follows. In section 2, we review the coupling-constant expression for the KE functional of the PD functional theory, and give an explicit form of the approximate KE functional [32]. In order to perform numerical calculations for the present scheme that includes the correlated TF functional, the self-consistent procedure is indispensable. We shall explain in section 3 the details of numerical calculations. The results and discussions are given in section 4. Finally, we present the concluding remarks in section 5.

2. Approximate form of the kinetic energy functional

In this section, we present the correlated TF functional that has been developed on the basis of the coupling-constant expression [32]. The coupling-constant expression for the KE functional $T[\gamma^{(2)}]$ is given by [32]

$$T[\gamma^{(2)}] = T_s[\gamma_{SD}^{(2)}[\gamma^{(2)}]] + \int_0^1 \langle \Psi_\lambda | \hat{W} - \hat{V}_{eff}^{int} | \Psi_\lambda \rangle_\Omega d\lambda - W[\gamma^{(2)}] - V_{eff}^{int}[\gamma_{SD}^{(2)}[\gamma^{(2)}]], \quad (1)$$

where $\gamma^{(2)}$ and $\gamma_{SD}^{(2)}[\gamma^{(2)}]$ denote the ground-state PDs of the real and noninteracting reference systems [27,29], respectively, and where \hat{W} is the operator of the electron-electron interaction energy, and where \hat{V}_{eff}^{int} is the effective potential of the electron-electron interaction in the noninteracting reference system [27,29]. In the right-hand side of (1), $T_s[\gamma_{SD}^{(2)}[\gamma^{(2)}]]$, $V_{eff}^{int}[\gamma_{SD}^{(2)}[\gamma^{(2)}]]$ and $W[\gamma^{(2)}]$ denote the ground-state KE of the noninteracting reference system, the expectation value of \hat{V}_{eff}^{int} with respect to the ground-state of the noninteracting reference system and the ground-state electron-electron interaction energy of the real system, respectively [32]. The second term of the right-hand side of (1) represents the coupling-constant integration. In this integration, $|\Psi_\lambda\rangle$ is the ground-state wave function for the Hamiltonian

$$\hat{H}_\lambda = \hat{T} + \hat{V}_{eff}^{int} + \hat{V} + \lambda(\hat{W} - \hat{V}_{eff}^{int}), \quad (2)$$

where \hat{T} and \hat{V} are operators of the KE and external potential energy, respectively, and where λ is the coupling constant. Equation (2) coincides with the Hamiltonian of the noninteracting reference system [27, 29] in the case of $\lambda = 0$ and coincides with that of the real system in the case of $\lambda = 1$.

In order to develop the approximate form of $T[\gamma^{(2)}]$, $|\Psi_\lambda\rangle$ is approximated by means of the perturbation theory. Namely, we take \hat{H}_0 and $\lambda(\hat{W} - \hat{V}_{eff}^{int})$ as the nonperturbative Hamiltonian and perturbation, respectively [32]. As the lowest-order approximation, by neglecting the second- and higher-order terms of $\hat{W} - \hat{V}_{eff}^{int}$, the coupling-constant expression (1) is approximated to [32]

$$T[\gamma^{(2)}] \approx T_s[\gamma_{SD}^{(2)}[\gamma^{(2)}]] - \left\{ W[\gamma^{(2)}] - W[\gamma_{SD}^{(2)}[\gamma^{(2)}]] \right\}, \quad (3)$$

where $W[\gamma_{SD}^{(2)}[\gamma^{(2)}]]$ is the expectation value of \hat{W} with respect to the ground state of the noninteracting reference system. Since $T_s[\gamma_{SD}^{(2)}[\gamma^{(2)}]]$ is the KE of the noninteracting system, it may be reasonably approximated by the TF functional, $T_{TF}[\rho]$ [42, 43], as an example. The magnitude of $W[\gamma^{(2)}] - W[\gamma_{SD}^{(2)}[\gamma^{(2)}]]$ of (3) is expected to be comparable to that of the correlation energy. Therefore, the second term may be approximated by the correlation energy functional of the LDA,

$E_c^{LDA}[\rho]$ [44], as an example. Thus, we get the approximate form:

$$T_{cTF}[\gamma^{(2)}] = T_{TF}[\rho] - E_c^{LDA}[\rho] \quad (4)$$

with

$$\rho(\mathbf{r}) = \frac{2}{N-1} \int \gamma^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r'. \quad (5)$$

Equation (4) is referred to as the correlated TF functional. The correlated TF functional is the first one that is developed on the basis of the coupling-constant expression for the KE functional [32].

3. Calculation method

In order to test the correlated TF functional, the atomic structure of the neutral Ne is calculated on the basis of the correction method that has recently been developed for the purpose of extending the search region of PDs [31]. The first step of this method is to prepare the *seed PD* that corresponds to the variationally best PD before extending the search region of PDs [31]. In order to prepare the seed PD, we employ as the search region the set of PDs that are constructed from the linear combination of the prescribed Slater determinants (SDs) [30]. If the coefficient of the linear combination is denoted by C_i , then the PDs that belong to the search region are expressed by

$$\gamma^{(2)}[\{C_i\}](\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') = \sum_i |C_i|^2 \gamma_{SSD,i}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') + \frac{1}{2} \sum_i \sum_{j \neq i} C_i^* C_j \Gamma_{i_1 j_1}^{ij}(\mathbf{r}\mathbf{r}') + \frac{1}{2} \sum_i \sum_{j \neq i} C_i^* C_j \Gamma_{i_1 i_2 j_1 j_2}^{ij}(\mathbf{r}\mathbf{r}') \quad (6)$$

with

$$\sum_i |C_i|^2 = 1, \quad (7)$$

where $\gamma_{SSD,i}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$ denotes the PD calculated from i -th SD, and where $\Gamma_{i_1 j_1}^{ij}(\mathbf{r}\mathbf{r}')$ and $\Gamma_{i_1 i_2 j_1 j_2}^{ij}(\mathbf{r}\mathbf{r}')$ correspond to the components which come from single and doubly-excitations, respectively. In (6), the symbol $i \neq j$ denotes that i -th SD is different from j -th SD by one constituent orbital. The symbol $i_1 (j_1)$ stands for the quantum number of such a different orbital of i -th (j -th) SD. In the same way, the symbol $i \neq j$ in (6) denotes that i -th SD is different from j -th SD by two constituent orbitals. The symbols i_1 and i_2 (j_1 and j_2) stand for the quantum numbers of such two different orbitals of i -th (j -th) SD. Note that $\gamma_{SSD,i}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}')$, $\Gamma_{i_1 j_1}^{ij}(\mathbf{r}\mathbf{r}')$ and $\Gamma_{i_1 i_2 j_1 j_2}^{ij}(\mathbf{r}\mathbf{r}')$ are determined by the prescribed SDs [30]. By changing C_i 's with keeping the condition (7), the PDs given by (6) vary within a set of N -representable PDs. With the aid of the Hohenberg-Kohn theorem with respect to the PD, we obtain the following equations for C_i 's in a similar way to the previous work [30]:

$$\sum_j A_{ij}[\{C_i\}] C_i = \mu C_i \quad (8)$$

with

$$A_{ij}[\{C_i\}] = \begin{cases} \iint \left\{ \frac{2}{N-1} f[\{C_i\}](\mathbf{r}) + \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}')}{N-1} \right\} \gamma_{SSD,i}^{(2)}(\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r d^3r' & (i = j) \\ \iint \left\{ \frac{1}{N-1} f[\{C_i\}](\mathbf{r}) + \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}')}{N-1} \right\} \Gamma_{i_1 j_1}^{ij}(\mathbf{r}\mathbf{r}') d^3r d^3r' & (i \neq j) \\ \iint \left\{ \frac{e^2}{|\mathbf{r}-\mathbf{r}'|} + \frac{v_{ext}(\mathbf{r}) + v_{ext}(\mathbf{r}')}{N-1} \right\} \Gamma_{i_1 j_1 j_2}^{ij}(\mathbf{r}\mathbf{r}') d^3r d^3r' & (i \neq j) \\ 0 & \text{otherwise} \end{cases} \quad (9)$$

Here, the function $f[\{C_i\}](\mathbf{r})$ is given by

$$f[\{C_i\}](\mathbf{r}) = (3\pi^2)^{2/3} \rho[\{C_i\}](\mathbf{r})^{2/3} - v_c^{LDA}[\rho[\{C_i\}]](\mathbf{r}) \quad (10)$$

with

$$\rho[\{C_i\}](\mathbf{r}) = \frac{2}{N-1} \iint \gamma^{(2)}[\{C_i\}](\mathbf{r}\mathbf{r}'; \mathbf{r}\mathbf{r}') d^3r' \quad (11)$$

where v_c^{LDA} denotes the correlation potential of the LDA. The solution C_i' 's of the above equations provides the variationally best PD, i.e., the seed PD.

Equations (8)–(11) should be solved in a self-consistent way. The flowchart of numerical calculations is shown in figure 1. First, we give initial values of C_i' 's. Then, matrix elements $A_{ij}[\{C_i\}]$ are calculated through (9). By diagonalizing $A_{ij}[\{C_i\}]$, we get a new set of C_i' 's. This

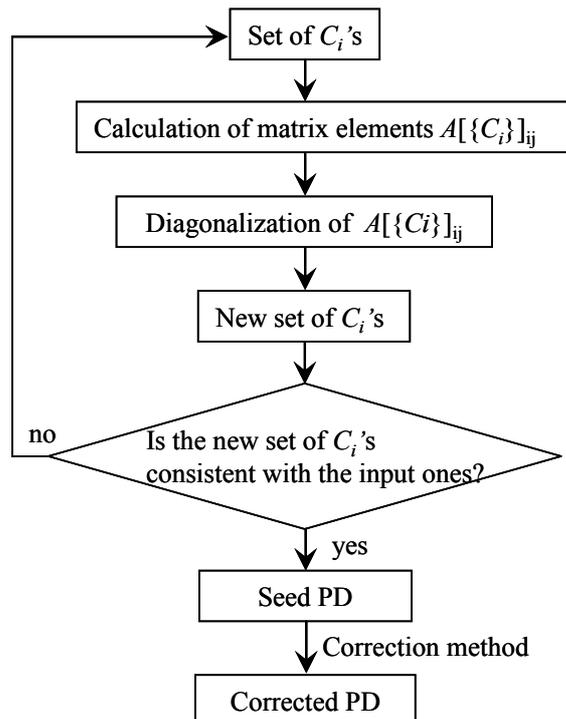


Figure 1. Flowchart of numerical calculations.

procedure is repeated until the input C_i' s are consistent with output ones. Thus, the coefficients that provide the seed PD are obtained.

Next, according to the correction method [31], the corrected PD, which corresponds to the variationally best PD after extending the search region of PDs, is calculated from the seed PD. By using the corrected PD, we evaluate errors of the KE, electron-electron interaction and potential energies, which are denoted by ΔT , ΔW and ΔV , respectively. These errors are calculated as the differences between the present results and the standard data. As the standard data, we use the results of the $1/Z$ expansion method [45] that is based on data of configuration interaction (CI) calculations and experiments [46].

4. Results of test calculations

Atomic structure calculations are performed for the neutral Ne atom. The virial ratio, ΔT , ΔW and ΔV are summarized in the first row of Tab. 1. For the purpose of reference, results that are calculated from the seed PD are also listed in the second row of Tab. 1 (without the correction).

It is found from Tab. 1 that the KE without the correction is lower than that of the CI method. This tendency is consistent with the fact that the usual TF functional is apt to underestimate the KE [47]. The KE, electron-electron interaction and potential energies change in a favorable way by means of the correction method. However, a certain amount of error remains in the KE, electron-electron interaction and potential energies. This means that there is a room for improvement in the approximate form of the KE functional.

Table 1. Errors of the KE, electron-electron interaction energy and potential energy that are denoted by ΔT , ΔW and ΔV , respectively, are shown together with the virial ratio. Results after (before) the correction method are shown in the first (second) row. The standard data of the KE, electron-electron interaction and potential energies are 257.874 (ryd.), 106.438 (ryd.) and -622.186 (ryd.), respectively [45].

	$\Delta T(\%)$	$\Delta W(\%)$	$\Delta V(\%)$	Virial ratio
Present results	7.922	2.634	7.208	-2.004
without the correction	-10.039	-6.344	-2.171	-2.161

It is also found that the virial ratio is much improved by the correction method. This is because the main component of the correlated TF functional, which is the usual TF functional $T_{TF}[\rho]$, satisfies the scaling property of the KE functional [48]. Therefore, we obtain the virial ratio that is close to the correct value -2.0.

It is well known that the atomic shell structure is absent in the profile of the electron density if the usual TF and related models are employed [47]. Figure 2 shows the profile of the electron density of the present scheme. The atomic shell structure clearly appears even though there remains the difference between the CI result [49] and the present one. This also seems to be an advantage of the present PD functional theory.

These test calculations are the first evaluations of the approximate KE functional that is developed on the basis of the coupling-constant expression. Therefore, calculation results obtained here are expected to be used as the reference data for comparison in developing more accurate functionals.

5. Concluding Remarks

In this paper, the validity of the correlated TF functional, which has recently been proposed for the KE functional of the PD functional theory on the basis of the coupling-constant expression, is checked by atomic structure calculations of the neutral Ne atom. Although it has been well known that the usual TF functional tends to underestimate the KE [47], the correlated TF functional inversely overestimates the KE by about 8 percent in our PD functional theory. The correction method [31] actually works toward reducing the errors, but there yet still remain some of them. This means that it is necessary to adopt or develop more appropriate functional as the noninteracting KE functional.

However, since this work is the first computational trial of the second strategy (ii) mentioned in section 1, the present results may become the reference data in judging whether the approximate form is valid or not. It can be said that we make the first but significant step toward developing the approximate KE functional which is based on the coupling-constant expression.

Using these reference data, in conjunction with the correction method [31], we will be able to improve on the approximate KE functional in future.

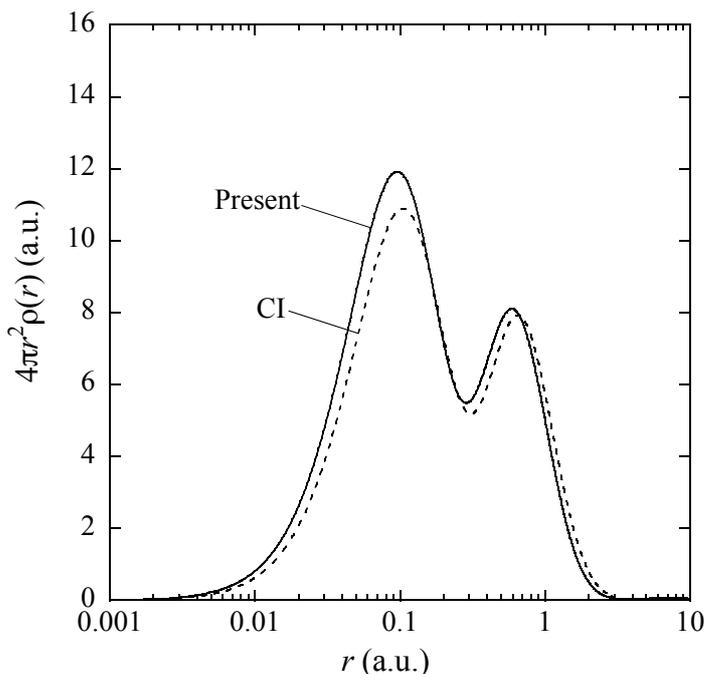


Figure 2. Profiles of the electron density of the neutral Ne atom. Solid and dashed lines denote the present and CI results[49], respectively.

Acknowledgements

This work was partially supported by Grants-in-Aid for Scientific Research (No. 22540390 and No. 23540446) of the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

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