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Comparison between the vorticity expansion approximation and the local density approximation of the current-density functional theory from the viewpoint of sum rules

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Abstract

We compare the vorticity expansion approximation (VEA) with the local density approximation (LDA) of the current-density functional theory from the viewpoint of sum rules. The VEA formulae satisfy all sum rules which are derived from uniform and nonuniform coordinate scaling properties, while the LDA formulae do not satisfy at least about a third of the sum rules. The validity of the VEA formula is thus confirmed successfully.

1. Introduction

The current-density functional theory (CDFT) [1, 2] is useful for describing the ground-state properties of systems such as open-shell atoms and inhomogeneous electronic systems in a magnetic field. The CDFT has been extended to the relativistic version, relativistic current- and spin-density functional theory (RCSDFT) [3, 4]. This relativistic version is also useful especially for f-electron materials where an orbital current is induced from both the strong spin-orbit interaction and the intra-atomic Coulomb interaction.

In order to perform actual calculations on the basis of such theories, the approximate form of the exchange–correlation energy functional is indispensable. There are two strategies for developing the approximate form [5, 6]. One is to start with the coupling-constant expression of the exchange–correlation energy functional. By using this exact expression, the local density approximation (LDA) of the CDFT has been proposed similarly to that in the density functional theory (DFT) [5, 6]. Another strategy is to utilize as constraints exact relations that are satisfied with the exchange and correlation energy functionals. This strategy has been successfully used in developing the generalized gradient approximation (GGA) [7, 8] of the DFT. For the exchange–correlation energy functional of the CDFT as well as that of the DFT, many kinds of

exact relations have been derived by means of the virial theorem, and uniform and nonuniform scaling properties [5, 6, 9].

According to the latter strategy, we have recently proposed the vorticity expansion approximation (VEA) for the exchange and correlation energy functionals [10] of the CDFT. The VEA formulae are constructed by utilizing exact relations as constraints [10]. Due to the well-behaved forms, the VEA formulae can well reproduce the exchange and correlation energies of the homogeneous electron liquid under a uniform magnetic field [10].

In this paper, for the purpose of evaluating the validity of the VEA formulae, we check whether or not the VEA formulae satisfy other sum rules which are not used in constructing the VEA formulae. For comparison, the LDA formulae are evaluated by means of sum rules, similarly to the VEA case.

2. VEA formulae of the exchange and correlation energy functionals of the CDFT

In the CDFT, the electron density $\rho(\mathbf{r})$ and paramagnetic current density $\mathbf{j}_p(\mathbf{r})$ are chosen as basic variables. The exchange–correlation energy functional is formally defined as [1, 2]

$$E_{xc}[\rho, \mathbf{j}_p] = F[\rho, \mathbf{j}_p] - T_s[\rho, \mathbf{j}_p] - U[\rho], \quad (1)$$

where $U[\rho]$, $F[\rho, \mathbf{j}_p]$ and $T_s[\rho, \mathbf{j}_p]$ are the Hartree energy term, the universal functional and the kinetic energy functional of the reference system, respectively. $F[\rho, \mathbf{j}_p]$ and $T_s[\rho, \mathbf{j}_p]$ are defined by using the constrained-search formulation [11–17]:

$$F[\rho, \mathbf{j}_p] = \text{Min}_{\Psi \rightarrow (\rho, \mathbf{j}_p)} \langle \Psi | \hat{T} + \hat{W} | \Psi \rangle =: \langle \Psi[\rho, \mathbf{j}_p] | \hat{T} + \hat{W} | \Psi[\rho, \mathbf{j}_p] \rangle, \quad (2)$$

$$T_s[\rho, \mathbf{j}_p] = \text{Min}_{\Phi \rightarrow (\rho, \mathbf{j}_p)} \langle \Phi | \hat{T} | \Phi \rangle =: \langle \Phi[\rho, \mathbf{j}_p] | \hat{T} | \Phi[\rho, \mathbf{j}_p] \rangle, \quad (3)$$

In equation (2), the minimizing is performed among antisymmetric wavefunctions Ψ that yield the prescribed $\rho(\mathbf{r})$ and $\mathbf{j}_p(\mathbf{r})$, and $\Psi[\rho, \mathbf{j}_p]$ means the minimizing wavefunction. Similarly, the minimizing in equation (3) is done among the single Slater determinants Φ that yield the prescribed $\rho(\mathbf{r})$ and $\mathbf{j}_p(\mathbf{r})$. $\Phi[\rho, \mathbf{j}_p]$ means the minimizing single Slater determinant. Substituting equations (2) and (3) into equation (1), we have

$$\begin{aligned} E_{xc}[\rho, \mathbf{j}_p] &= \langle \Phi[\rho, \mathbf{j}_p] | \hat{W} | \Phi[\rho, \mathbf{j}_p] \rangle - U[\rho] \\ &\quad + \langle \Psi[\rho, \mathbf{j}_p] | \hat{W} | \Psi[\rho, \mathbf{j}_p] \rangle - \langle \Phi[\rho, \mathbf{j}_p] | \hat{W} | \Phi[\rho, \mathbf{j}_p] \rangle \\ &\quad + \langle \Psi[\rho, \mathbf{j}_p] | \hat{T} | \Psi[\rho, \mathbf{j}_p] \rangle - \langle \Phi[\rho, \mathbf{j}_p] | \hat{T} | \Phi[\rho, \mathbf{j}_p] \rangle. \end{aligned} \quad (4)$$

Let us define the exchange energy functional $E_x[\rho, \mathbf{j}_p]$ as the first two terms on the right-hand side of equation (4), and the correlation energy functional $E_c[\rho, \mathbf{j}_p]$ as the remaining four terms, i.e.,

$$E_x[\rho, \mathbf{j}_p] := \langle \Phi[\rho, \mathbf{j}_p] | \hat{W} | \Phi[\rho, \mathbf{j}_p] \rangle - U[\rho], \quad (5)$$

$$\begin{aligned} E_c[\rho, \mathbf{j}_p] &:= \langle \Psi[\rho, \mathbf{j}_p] | \hat{W} | \Psi[\rho, \mathbf{j}_p] \rangle - \langle \Phi[\rho, \mathbf{j}_p] | \hat{W} | \Phi[\rho, \mathbf{j}_p] \rangle \\ &\quad + \langle \Psi[\rho, \mathbf{j}_p] | \hat{T} | \Psi[\rho, \mathbf{j}_p] \rangle - \langle \Phi[\rho, \mathbf{j}_p] | \hat{T} | \Phi[\rho, \mathbf{j}_p] \rangle. \end{aligned} \quad (6)$$

These definitions are the same as those previously given by Erhard and Gross [9].

In recent years, we have proposed a practical form of the exchange–correlation energy functional of the CDFT [10]. Both $E_x[\rho, \mathbf{j}_p]$ and $E_c[\rho, \mathbf{j}_p]$ are expanded in terms of the vorticity of the paramagnetic current density that is defined by

$$\mathbf{v}(\mathbf{r}) := \nabla \times \{ \mathbf{j}_p(\mathbf{r}) / \rho(\mathbf{r}) \}. \quad (7)$$

Table 1. Comparison of the VEA and the LDA defined in [5]. As regards several sum rules, we cannot conclude whether they are satisfied by the LDA formulae or not, which are marked by ‘—’. These ambiguities will be removed by studying more the homogeneous electron liquid under the weak magnetic field, especially, in the cases of high- and low-density limits [19].

No.	Sum rule	CDFT-LDA	VEA
1	$E_x[\rho_\lambda, \mathbf{j}_p^\lambda] = \lambda E_x[\rho, \mathbf{j}_p]$	Yes	Yes
2	$E_c[\rho_\lambda, \mathbf{j}_p^\lambda] \geq \lambda E_c[\rho, \mathbf{j}_p], \lambda \geq 1$	Yes	Yes
3	$E_c[\rho_\lambda, \mathbf{j}_p^\lambda] \leq \lambda E_c[\rho, \mathbf{j}_p], \lambda \leq 1$	Yes	Yes
4	$\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda^x, \mathbf{j}_{p\lambda}^x] = 0$	—	Yes
5	$\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_\lambda^x, \mathbf{j}_{p\lambda}^x] = \text{const}$	—	Yes
6	$\lim_{\lambda \rightarrow 0} E_c[\rho_\lambda^x, \mathbf{j}_{p\lambda}^x] = 0$	Yes	Yes
7	$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[\rho_\lambda^x, \mathbf{j}_{p\lambda}^x] = 0$	No	Yes
8	$\lim_{\lambda \rightarrow 0} \lambda^{-2} E_c[\rho_\lambda^x, \mathbf{j}_{p\lambda}^x] = \text{const}$	No	Yes
9	$\lim_{\lambda \rightarrow \infty} E_c[\rho_{\lambda\lambda}^{xy}, \mathbf{j}_{p\lambda\lambda}^{xy}] = 0$	—	Yes
10	$\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_{\lambda\lambda}^{xy}, \mathbf{j}_{p\lambda\lambda}^{xy}] = \text{const}$	—	Yes
11	$\lim_{\lambda \rightarrow 0} E_c[\rho_{\lambda\lambda}^{xy}, \mathbf{j}_{p\lambda\lambda}^{xy}] = 0$	Yes	Yes
12	$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[\rho_{\lambda\lambda}^{xy}, \mathbf{j}_{p\lambda\lambda}^{xy}] = 0$	No	Yes
13	$\lim_{\lambda \rightarrow 0} \lambda^{-2} E_c[\rho_{\lambda\lambda}^{xy}, \mathbf{j}_{p\lambda\lambda}^{xy}] = \text{const}$	No	Yes
14	$\lim_{\lambda \rightarrow \infty} E_c[\rho_{\lambda\lambda\lambda-1}^{xyz}, \mathbf{j}_{p\lambda\lambda\lambda-1}^{xyz}] = 0$	—	Yes
15	$\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_{\lambda\lambda\lambda-1}^{xyz}, \mathbf{j}_{p\lambda\lambda\lambda-1}^{xyz}] = 0$	—	Yes
16	$\lim_{\lambda \rightarrow \infty} \lambda^2 E_c[\rho_{\lambda\lambda\lambda-1}^{xyz}, \mathbf{j}_{p\lambda\lambda\lambda-1}^{xyz}] = \text{const}$	—	Yes
17	$\lim_{\lambda \rightarrow 0} E_c[\rho_{\lambda\lambda\lambda-1}^{xyz}, \mathbf{j}_{p\lambda\lambda\lambda-1}^{xyz}] = 0$	Yes	Yes
18	$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[\rho_{\lambda\lambda\lambda-1}^{xyz}, \mathbf{j}_{p\lambda\lambda\lambda-1}^{xyz}] = 0$	No	Yes
19	$\lim_{\lambda \rightarrow 0} \lambda^{-2} E_c[\rho_{\lambda\lambda\lambda-1}^{xyz}, \mathbf{j}_{p\lambda\lambda\lambda-1}^{xyz}] = \text{const}$	No	Yes
20	$\lim_{\lambda \rightarrow \infty} E_c[\rho_\lambda^z, \mathbf{j}_{p\lambda}^z] = 0$	No	Yes
21	$\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_\lambda^z, \mathbf{j}_{p\lambda}^z] = \text{const}$	No	Yes
22	$\lim_{\lambda \rightarrow 0} E_c[\rho_\lambda^z, \mathbf{j}_{p\lambda}^z] = 0$	—	Yes
23	$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[\rho_\lambda^z, \mathbf{j}_{p\lambda}^z] = 0$	—	Yes
24	$\lim_{\lambda \rightarrow 0} \lambda^{-2} E_c[\rho_\lambda^z, \mathbf{j}_{p\lambda}^z] = \text{const}$	—	Yes
25	$\lim_{\lambda \rightarrow \infty} E_c[\rho_{\lambda\lambda}^{yz}, \mathbf{j}_{p\lambda\lambda}^{yz}] = 0$	No	Yes
26	$\lim_{\lambda \rightarrow \infty} \lambda E_c[\rho_{\lambda\lambda}^{yz}, \mathbf{j}_{p\lambda\lambda}^{yz}] = \text{const}$	No	Yes
27	$\lim_{\lambda \rightarrow 0} E_c[\rho_{\lambda\lambda}^{yz}, \mathbf{j}_{p\lambda\lambda}^{yz}] = 0$	—	Yes
28	$\lim_{\lambda \rightarrow 0} \lambda^{-1} E_c[\rho_{\lambda\lambda}^{yz}, \mathbf{j}_{p\lambda\lambda}^{yz}] = 0$	—	Yes
29	$\lim_{\lambda \rightarrow 0} \lambda^{-2} E_c[\rho_{\lambda\lambda}^{yz}, \mathbf{j}_{p\lambda\lambda}^{yz}] = \text{const}$	—	Yes

The expansions are taken up to the second order of the vorticity, and the expansion coefficients are determined by requiring them to satisfy the first 19 sum rules [5, 6, 9] of table 1. Resultant VEA formula of the exchange energy functional is given by [10]

$$\bar{E}_x[\rho, \mathbf{v}] = E_x[\rho] + \int \rho(\mathbf{r}) |\mathbf{v}(\mathbf{r})|^2 D(\rho)|_{\rho=\rho(\mathbf{r})} \mathbf{dr}, \quad (8)$$

where $E_x[\rho]$ is the exchange energy functional of the conventional DFT. $D(\rho)$ is expressed as the power of ρ , i.e.,

Table 2. The values of dimensionless constants in the VEA formulae. The values are determined by fitting the VEA formulae to the exchange and correlation energies of the homogeneous electron liquid under the uniform magnetic field [18].

\bar{D}_x	\bar{C}_0	$\bar{\alpha}$	$\bar{\delta}$
3.76×10^{-4}	-4.67×10^{-4}	0.65	1.0×10^{-30}

$$D(\rho) = \frac{\bar{D}_x \hbar^2}{a_H^3 \varepsilon_H} \rho^{-1}, \quad (9)$$

where \bar{D}_x is the dimensionless constant, and a_H and ε_H stand for the Bohr radius and Rydberg constant, respectively.

Also, the VEA formula of the correlation energy functional is given by [10]

$$\bar{E}_c[\rho, \mathbf{v}] = E_c[\rho] + \int \rho(\mathbf{r}) |\mathbf{v}(\mathbf{r})|^2 C(\rho)|_{\rho=\rho(\mathbf{r})} \mathbf{d}\mathbf{r}, \quad (10)$$

where $E_c[\rho]$ is the correlation energy functional of the conventional DFT. The expansion coefficient $C(\rho)$ has been devised so that equation (10) satisfies the first 19 sum rules of table 1 as much as possible. Our best expression of $C(\rho)$ is given by [10]

$$C(\rho) = \bar{C}_0 \frac{\hbar^2}{a_H^3 \varepsilon_H} \frac{e^{-\bar{\alpha} a_H^3 \rho}}{(\rho - \bar{\delta}/a_H^3)^3}, \quad (11)$$

where \bar{C}_0 , $\bar{\alpha}$ and $\bar{\delta}$ are dimensionless constants. If we choose $\bar{C}_0 < 0$, $\bar{\alpha} > 0$ and $0 < \bar{\delta} \ll a_H^3 \rho$, then the first 19 sum rules of table 1 are satisfied with equations (10) and (11).

The values of \bar{D}_x , \bar{C}_0 , $\bar{\alpha}$ and $\bar{\delta}$ are determined by requiring that the VEA formulae in the uniform limit reproduce the exchange ($\varepsilon_x^{\text{homo}}$) and correlation energies ($\varepsilon_c^{\text{homo}}$) of the homogeneous electron liquid under a uniform magnetic field. The VEA formulae in the uniform limit are in good agreement with the results of Takada and Goto [18]. The resultant values of \bar{D}_x , \bar{C}_0 , $\bar{\alpha}$ and $\bar{\delta}$ are summarized in table 2.

3. Checking the validity of the VEA formulae

As mentioned in the previous section, the VEA formulae in the uniform limit can well reproduce $\varepsilon_x^{\text{homo}}$ and $\varepsilon_c^{\text{homo}}$. This implies the validity of the VEA formulae. In order to confirm the validity of the VEA formulae in more detail, we shall compare the VEA formulae with the LDA formulae from the viewpoint of sum rules satisfied. In addition to 19 sum rules which have been utilized in constructing the VEA formulae [10], we shall further check whether the VEA and LDA formulae satisfy other sum rules or not. These investigations are performed under the assumption that the magnetic field is parallel to the x -direction. The LDA formulae used here are defined on the basis of the results which have been calculated within the random phase approximation [19]. The results are summarized in table 1. Note that ambiguities in satisfaction or not of several sum rules by the LDA formulae (the third column in table 1) are due to the insufficient knowledge about the exchange and correlation energy of the homogeneous electron liquid under a uniform magnetic field.

The VEA formulae satisfy all sum rules while the LDA formulae do not satisfy at least a third of sum rules which are marked ‘no’ in table 1. It is fair to say that the VEA formulae have well-behaved forms in comparison with the LDA formulae. Note that even though the VEA formulae satisfy more sum rules than the LDA, the VEA formulae would not always give quantitatively better results than the LDA formulae. The sum rule does not always guarantee

to make a good energy functional. However, to say the least of it, the sum rule may fairly well get rid of the difficulties which lead to nonphysical results, from the approximate functional. In this sense, it can be expected that the present VEA formulae may lead to more reasonable results than the LDA.

Finally, we shall give a brief comment on the direction of the magnetic field. If the magnetic field is parallel to the z -axis, we may obtain different results for the LDA formulae. In this case, the first three sum rules are satisfied by the LDA formulae similarly to the above case (x -direction), while the 6th, 11th, 17th sum rules are not satisfied. Instead, the 22nd and 27th sum rules are satisfied with the LDA formulae. As contrasted with such a direction dependence of the LDA, the VEA formulae correctly satisfy all sum rules regardless of the direction of the magnetic field. Such correct behaviour also supports the advantage of the VEA over the LDA.

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