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Parameter-free exchange functional

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Conventional generalized-gradient approximations for exchange energy are derived to obey the fundamental conditions of the exact exchange functional. We present a simple analytic exchange functional that does not contain a semiempirical parameter or an adjusted fundamental constant. We show that this functional satisfies several significant and strict fundamental conditions, and gives accurate exchange energies for the atoms, hydrogen through argon, within a margin of error of a few percent. It can be updated for any kind of kinetic-energy density. Surprisingly, the present formalism exactly gives the gradient expansion coefficient for slowly varying density.

I. INTRODUCTION

Density-functional theory (DFT) is widely used as a self-consistent-field approach that approximates exchange-correlation energy by using a functional of the electron density based on a physical model. In a recent paper,[1] we indicated that the reliability of a functional depends on whether it (1) obeys the conditions of the exact functional, (2) is applicable to a wide class of problems and a wide variety of systems, (3) has a simple form with a minimum number of parameters (including fundamental constants), (4) contains no additional part for obtaining specific properties, and (5) has a progressive form that can be updated. The one-parameter progressive functional[1,2] was developed as a correlation functional that satisfies all these criteria. However, almost all conventional generalized-gradient-approximation (GGA) exchange functionals were derived to reproduce specific properties with supplementary functions and adjusted fundamental constants.[3–5] This may cause serious deficiencies in the description of some kinds of physical situations. For example, it was been pointed out that a complicated form often leads to spurious wiggles in the exchange potential.[5] Many believe that a parametrized functional is necessary to provide practical exchange energies. We must ask ourselves if this is really the case.

In Sec. II, we introduce a simple analytic exchange functional that contains neither a semiempirical parameter nor an adjusted fundamental constant. The functional is numerically investigated by calculating the exchange energies of atoms in Sec. III. We also examine it from a physical point of view by applying it to the conditions of the exact exchange functional in Sec. IV. The advantages and disadvantages of the functional are discussed in Sec. V.

II. THEORY

The density-matrix-expansion (DME) scheme[6–8] may be one of the best strategies for developing an analytical exchange functional. According to this scheme, a spin-polarized Hartree-Fock (HF) first-order density matrix for σ-spin electrons is expanded by using spherical Bessel functions j_n up to second order, as shown by[6]

$$P_{1\sigma}^{DME}\left(\mathbf{R}+\frac{\mathbf{r}}{2},\mathbf{R}-\frac{\mathbf{r}}{2}\right)=\frac{3j_1(k_\sigma r)}{k_\sigma r}\rho_\sigma(\mathbf{R})+\frac{35j_3(k_\sigma r)}{2k_\sigma^3 r}\left(\frac{\nabla^2\rho_\sigma(\mathbf{R})}{4}-\tau_\sigma(\mathbf{R})+\frac{3}{5}k_\sigma^2\rho_\sigma(\mathbf{R})\right)+\cdots, \tag{1}$$

where $r=|\mathbf{r}_i-\mathbf{r}_j|$ and $\mathbf{R}=(\mathbf{r}_i+\mathbf{r}_j)/2$ for each electron pair (i,j). Atomic units are used ($\hbar=e^2=m=1$, energies are in hartree and distances in bohr). The Fermi momentum $k_{F\sigma}=(6\pi^2\rho_\sigma)^{1/3}$ is substituted for the averaged relative momentum of two electrons, k_σ. The kinetic-energy density τ_σ is defined in the form of the HF noninteracting kinetic energy,

$$T_s=\frac{1}{2}\sum_\sigma\int\sum_i^{occ}|\nabla\psi_{i\sigma}|^2d^3\mathbf{R}=\frac{1}{2}\sum_\sigma\int\tau_\sigma d^3\mathbf{R}. \tag{2}$$

By using Eq. (1), the DME of the HF exchange energy becomes[7]

$$E_x^{DME}[\rho_\sigma,k_\sigma,\tau_\sigma]=-\frac{1}{2}\sum_\sigma\int\frac{|P_{1\sigma}^{DME}(\mathbf{R}+\mathbf{r}/2,\mathbf{R}-\mathbf{r}/2)|^2}{r}d^3\mathbf{R}d^3\mathbf{r}\cong-\frac{\pi}{2}\sum_\sigma\int\left[\frac{9}{k_\sigma^2}\rho_\sigma^2+\frac{35}{3k_\sigma^4}\rho_\sigma\left(\frac{\nabla^2\rho_\sigma}{4}-\tau_\sigma+\frac{3}{5}k_\sigma^2\rho_\sigma\right)\right]d^3\mathbf{R}. \tag{3}$$

To eliminate the Laplacian of the density $\nabla^2\rho_\sigma$, the most difficult term to integrate, Eq. (3) is changed by a partial integration into[8]

$$E_x^{DME}[\rho_\sigma,k_\sigma,\tau_\sigma]=-\frac{\pi}{2}\sum_\sigma\int\left[\frac{9}{k_\sigma^2}\rho_\sigma^2+\frac{35}{3k_\sigma^4}\rho_\sigma^{8/3}\left(\frac{x_\sigma^2}{12}-z_\sigma\right)\right]d^3\mathbf{R}, \tag{4}$$

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where x_σ and z_σ are dimensionless parameters that can be expressed as $x_\sigma = |\nabla \rho_\sigma| / \rho_\sigma^{4/3}$, and $z_\sigma = (\tau_\sigma - 3k_\sigma^2 \rho_\sigma / 5) / \rho_\sigma^{5/3}$. The momentum k_σ is corrected from $k_{F\sigma}$ by using the adjustable parameter α, as $k_\sigma = k_{F\sigma}(1 + \alpha x_\sigma^2)$ or $k_\sigma = k_{F\sigma}\sqrt{1 + \alpha z_\sigma}$. These α terms are supplemented to obtain accurate exchange energies and fundamental properties.

The momentum k_σ has so far been regarded as an entirely arbitrary quantity that has the dimensions of inverse length.[8] However, according to the original paper on DME,[6] k_σ must be essentially the relative momentum at each center-of-mass coordinate **R** that is averaged over the momentum space. In this paper we express k_σ as a functional of the kinetic-energy density $\tau_\sigma(\mathbf{R})$ naturally, by explicitly determining the relation, such that

$$\tau_\sigma(\mathbf{R}) = 2\left\langle \frac{\mathbf{k}^2}{2} \right\rangle \rho_\sigma(\mathbf{R}) = \frac{\int \mathbf{k}^2 f_\sigma(\mathbf{R},\mathbf{k}) d^3\mathbf{k}}{\int f_\sigma(\mathbf{R},\mathbf{k}) d^3\mathbf{k}} \rho_\sigma(\mathbf{R})$$

$$= \frac{3}{5} k_\sigma^2(\mathbf{R}) \rho_\sigma(\mathbf{R}). \qquad (5)$$

In Eq. (5), the distribution function[9] $f_\sigma(\mathbf{R},\mathbf{k})$, for the spin-polarized first-order density matrix in Eq. (1), is approximated by using the step function $\Theta(k_\sigma - |\mathbf{k}|)$ in the momentum space on the ground of the Fourier transformation formula of the first term, $3j_1(k_\sigma r)\rho_\sigma / k_\sigma r$, such that

$$f_\sigma(\mathbf{R},\mathbf{k}) = \frac{1}{(2\pi)^3} \int P_{1\sigma}^{DME}\left(\mathbf{R} + \frac{\mathbf{r}}{2}, \mathbf{R} - \frac{\mathbf{r}}{2}\right) \exp(-i\mathbf{k}\cdot\mathbf{r}) d^3\mathbf{r}$$

$$\approx \text{const } \rho_\sigma(\mathbf{R}) \Theta(k_\sigma - |\mathbf{k}|). \qquad (6)$$

It is physically justified to substitute k_σ in Eq. (5) for that in the DME, because the averaged relative momentum is thought to be identical to the center-of-mass momentum that is calculated by the kinetic-energy density at the position. From Eq. (5), k_σ can be written inversely as

$$k_\sigma = \sqrt{\frac{5\tau_\sigma}{3\rho_\sigma}}. \qquad (7)$$

If τ_σ is equal to the Thomas-Fermi (TF) kinetic-energy density, $\tau_\sigma^{TF} = (3/5)(6\pi^2)^{2/3}\rho_\sigma^{5/3}$, k_σ becomes identical to $k_{F\sigma} = (6\pi^2\rho_\sigma)^{1/3}$ for the noninteracting system. Substituting Eq. (7) into Eq. (4) gives a simple τ_σ-dependent DME exchange functional:

$$E_x^{new}[\rho_\sigma, \nabla\rho_\sigma, \tau_\sigma] = -\frac{1}{2} \sum_\sigma \int \frac{27\pi}{5\tau_\sigma} \rho_\sigma^3 \left[1 + \frac{7x_\sigma^2 \rho_\sigma^{5/3}}{108\tau_\sigma}\right] d^3\mathbf{R}. \qquad (8)$$

We emphasize that this functional contains no adjusted parameter and no additional part for obtaining specific properties. If τ_σ is equal to τ_σ^{TF}, and the gradient of the density $\nabla\rho_\sigma$ is zero, Eq. (8) perfectly reproduces the local-spin-density approximation (LSDA) for the exchange energy.[10] The higher-order terms are neglected in Eq. (8),[11] because it may be hard to obtain stable values of $(x_\sigma^2/\tau_\sigma)^n$ for $n \geqslant 2$ in the numerical computation.

It is interesting to note that Ernzerhof and Scuseria[12] recently proposed the local τ approximation (LTA) that, contrary to Eq. (8), the lowest-order term in the expansion of E_x is proportional to $\tau^{4/5}$,

$$E_x^{LTA}[\tau] = C_x \int \left(\frac{\tau}{C_F}\right)^{4/5} d^3\mathbf{R}, \qquad (9)$$

where $C_x = -(3/4)(3/\pi)^{1/3}$ and $C_F = (3/10)(3\pi^2)^{2/3}$. The LTA also gives the LSDA exchange energy by substituting the TF kinetic-energy density into τ. However, it is clear that it may not reproduce the dimension of exchange energy in contrast with Eq. (8), unless the density can be expressed as a functional of only the kinetic-energy density such as in a system of slowly varying density.[12]

A criticism of Eq. (7) may be that a similar formulation was already suggested for k_σ by an analogy to classical thermodynamics for ideal gas.[8,10,13,14] The momentum $k_\sigma = \sqrt{(\tau_\sigma - \nabla^2\rho_\sigma/4)/3\rho_\sigma}$ is derived by using the Maxwell-Boltzmann distribution function and the kinetic-energy density for ideal gas. Recall that electron gas, in contrast to ideal gas, constitutes a Fermi sphere in the momentum space. The distribution function for electron gas therefore resembles $\rho_\sigma(\mathbf{R})\Theta(k_\sigma - |\mathbf{k}|)$ rather than the Maxwell-Boltzmann one, and the kinetic-energy density must be 3/5 times the ideal-gas one. Moreover, the Laplacian $\nabla^2\rho_\sigma$ term is an additional term that does not contribute to the kinetic energy, because it is artificially introduced by making use of the relation[10,14] $\int \nabla^2 \rho_\sigma d^3\mathbf{R} = 0$.

The exchange functional, [Eq. (8)], has a progressive part that can be updated for any kind of kinetic-energy density τ_σ. It is also useful to examine various approximations that have been analytically derived,[10] e.g., the Weizsäcker correction for the TF kinetic energy density up to the second-order (TFW),

$$\tau_\sigma^{TFW} = \tau_\sigma^{TF} + \frac{1}{36} \frac{|\nabla\rho_\sigma|^2}{\rho_\sigma}, \qquad (10)$$

and the Hodges correction up to the fourth-order (TFWH),

$$\tau_\sigma^{TFWH} = \tau_\sigma^{TFW} + \frac{1}{270(6\pi^2)^{2/3}} \left(\frac{|\nabla^2\rho_\sigma|^2}{\rho_\sigma^{5/3}} - \frac{9}{8} \frac{\nabla^2\rho_\sigma |\nabla\rho_\sigma|^2}{\rho_\sigma^{8/3}} \right.$$

$$\left. + \frac{1}{3} \frac{|\nabla\rho_\sigma|^4}{\rho_\sigma^{11/3}} \right). \qquad (11)$$

The sixth-order term gradient correction is reported to diverge for atoms.[10]

III. CALCULATIONS

Let us examine the exchange functional for some types of kinetic-energy density by calculating the exchange energies of atoms, H through Ar, with the Clementi HF Slater-type orbitals.[15] For numerical integration, we use a 50-point Euler-Maclaurin quadrature[16,17] for radial grids, and a 194-point Lebedev quadrature[18] for angular ones. For the exact values, we adopted exchange energies calculated by using the numerical HF method.[19] For τ_σ in Eq. (8), we will examine three types of approximated kinetic-energy densities—τ_σ^{TF} (TF-τ_σ), τ_σ^{TFW} (TFW-τ_σ), and τ_σ^{TFWH}

TABLE I. Calculated exchange energies for the ground states of atoms in hartree. The exact exchange energies are calculated by the numerical Hartree-Fock method (Ref. 19). HF-$\tau_\sigma^{(1)}$ is the first term of HF-τ_σ.

Atom	State	Exact	HF-$\tau_\sigma^{(1)}$	HF-τ_σ	TF-τ_σ	TFW-τ_σ	TFWH-τ_σ
H	^{2}S	−0.313	−0.337	−0.425	−0.399	−0.295	−0.290
He	^{1}S	−1.026	−0.981	−1.236	−1.311	−0.980	−0.962
Li	^{2}S	−1.781	−1.781	−2.235	−2.224	−1.703	−1.664
Be	^{1}S	−2.667	−2.673	−3.346	−3.248	−2.564	−2.498
B	^{2}P	−3.748	−3.649	−4.526	−4.471	−3.620	−3.540
C	^{3}P	−5.049	−4.887	−5.993	−5.928	−4.909	−4.818
N	^{4}S	−6.597	−6.465	−7.829	−7.644	−6.449	−6.347
O	^{3}P	−8.182	−7.779	−9.365	−9.356	−8.027	−7.922
F	^{2}P	−10.011	−9.449	−11.295	−11.349	−9.867	−9.758
Ne	^{1}S	−12.108	−11.532	−13.673	−13.624	−11.979	−11.864
Na	^{2}S	−14.018	−13.335	−15.746	−15.664	−13.860	−13.726
Mg	^{1}S	−15.994	−15.166	−17.848	−17.746	−15.830	−15.673
Al	^{2}P	−18.072	−17.081	−20.035	−19.971	−17.885	−17.715
Si	^{3}P	−20.284	−19.173	−22.412	−22.339	−20.078	−19.895
P	^{4}S	−22.641	−21.486	−25.025	−24.859	−22.417	−22.220
S	^{3}P	−25.006	−23.605	−27.428	−27.360	−24.766	−24.556
Cl	^{2}P	−27.517	−25.939	−30.060	−30.032	−27.267	−27.045
Ar	^{1}S	−30.185	−28.539	−32.978	−32.866	−29.923	−29.688
Mean percentage		—	96.525	116.085	115.294	97.820	96.493
Mean absolute Δ		—	0.633	1.459	1.400	0.154	0.279

(TFWH-τ_σ)—in addition to τ_σ^{HF} in Eq. (2) (HF-τ_σ).

Table I summarizes the calculated and HF exchange energies for the ground state of atoms. As the table indicates, Eq. (8) provides 10–20 % higher exchange energies for τ_σ^{HF}, energies similar to those for τ_σ^{TF}. The first term in τ_σ^{HF} provides much higher atomic exchange energies than does the LSDA exchange functional that corresponds to the first term in τ_σ^{TF}.[20] This may be due to the delocalization of τ_σ^{HF} relative to the electron density ρ_σ, because $\tau_\sigma^{TF}/\tau_\sigma^{HF}$ has been regarded as an indicator of nonlocality.[21] Compared with approximated energies, TFW-τ_σ results in more accurate exchange energies with errors of only a few percent. This seems to be a result of the employed kinetic-energy density values. Actually, τ_σ^{TFW} provides kinetic energies that are closer to the exact values.[10] The accuracy of TFW-τ_σ suggests that a GGA-type kinetic-energy density may be suited to the DME scheme because of the similarity in the fundamental physical models.

IV. FUNDAMENTAL CONDITIONS

In a recent paper,[20] we summarized some significant and strict conditions in the exchange energy for K_σ:

$$E_x = -\frac{1}{2}\sum_\sigma \int \rho_\sigma^{4/3} K_\sigma d^3\mathbf{R}. \tag{12}$$

The K_σ term for the exchange functional in Eq. (8) is expressed as

$$K_\sigma^{new} = \frac{27\pi}{5\tau_\sigma}\rho_\sigma^{5/3}\left[1+\frac{7x_\sigma^2\rho_\sigma^{5/3}}{108\tau_\sigma}\right]. \tag{13}$$

We performed investigations to make sure K_σ^{new} satisfies these conditions. In Table II, we indicate the conditions met by K_σ^{new} for τ_σ^{HF} ($K_\sigma^{HF\text{-}\tau_\sigma}$) and for τ_σ^{TFW} ($K_\sigma^{TFW\text{-}\tau_\sigma}$). The K_σ value, of Becke (B88),[3] Perdew-Wang (PW91),[4] and Perdew-Burke-Ernzerhof[5] (PBE) functionals are also examined.

(A) K_σ keeps within the bounds of $0 < K_\sigma < 4.231$ (the electron correlation effect is not taken into account).[22,23] The value of $K_\sigma^{TFW\text{-}\tau_\sigma}$ does not go beyond these bounds, because, as x_σ increases from zero to ∞, it increases from 1.861, the value of the LSDA exchange functional, to $(25/7)(3/4\pi)^{1/3} = 2.216$ at $x_\sigma = (6/5)6^{5/6}\pi^{2/3} = 11.457$, and then decreases monotonically to zero. We found that $K_\sigma^{HF\text{-}\tau_\sigma}$ sometimes exceeds these bounds.

(B) For coordinate scaling λ, K_σ is scaled as[24] (a) a constant under uniform scaling, and in high- and low-density limits; (b) $O(\lambda^{1/3})$ under nonuniform scaling of the x and y coordinates; and (c) $O(\lambda^{-1/3})$ under nonuniform scaling of the x coordinate. The uniform scaling condition (a) is satisfied by $K_\sigma^{HF\text{-}\tau_\sigma}$ and $K_\sigma^{TFW\text{-}\tau_\sigma}$, because both τ_σ^{HF} and τ_σ^{TFW} are scaled as $\lambda^5\tau_\sigma$, and follow the condition for the noninteracting kinetic energy,[24] $T_s[\rho_\lambda] = \lambda^2 T_s[\rho]$. However, $K_\sigma^{TFW\text{-}\tau_\sigma}$ does not satisfy nonuniform scaling conditions (b) and (c) because of the erroneous λ dependency of τ_σ^{TFW}: $O(\lambda^{-2/3})$ for the low-density limit and $O(\lambda^{4/3})$ for the high-density limit. For $K_\sigma^{HF\text{-}\tau_\sigma}$, we cannot determine the λ dependency, because there is no equality for the nonuniform scaling of τ_σ.[25]

(C) K_σ reproduces that of the LSDA exchange functional (K_σ^{LSDA}) for constant density. The kinetic-energy densities, including τ_σ^{HF} and τ_σ^{TFW}, decrease to τ_σ^{TF} at this limit. K_σ^{new} is therefore identical with K_σ^{LSDA} at a constant density.

TABLE II. Some strict physical conditions for K_σ in the exact exchange functional, $E_x = -(1/2)\Sigma_\sigma \int \rho_\sigma^{4/3} K_\sigma d^3\mathbf{R}$. The present exchange functionals (TFW-τ_σ and HF-τ_σ) are compared with approximate exchange functionals (Refs. 3–5 and 10). In condition (B), λ is a coordinate-scaling parameter. Condition (D) indicates $\lim_{x_\sigma \to 0} K_\sigma = 3(3/4\pi)^{1/3}[1 + \{5/81(6\pi^2)^{2/3}\} x_\sigma^2 + O(x_\sigma^4)]$, and the gradient expansion coefficient is the conventional $5/162(6\pi^2)^{2/3}$. The PBE functional contains a linear-response term. In condition (E), ρ_1 is the density for a one-electron system. The B88 functional obeys condition (F) only for exponential ρ.

Conditions	LSDA	B88	PW91	PBE	TFW-τ_σ	HF-τ_σ
(A) $0 < K_\sigma < 4.231$	Yes	No	Yes	Yes	Yes	No
(B-a) $K_\sigma[\rho_\lambda] = \text{const}$	Yes	Yes	Yes	Yes	Yes	Yes
(B-b) $\lim_{\lambda \to 0,\infty} K_\sigma[\rho_{\lambda\lambda}^{xy}] = O(\lambda^{1/3})$	No	No	No	No	No	—
(B-c) $\lim_{\lambda \to 0,\infty} K_\sigma[\rho_\lambda^{x}] = O(\lambda^{-1/3})$	No	No	No	No	No	—
(C) $K_\sigma = 3(3/4\pi)^{1/3}$ for constant ρ	Yes	Yes	Yes	Yes	Yes	Yes
(D) GEA limit for slowly varying ρ	—	No	Yes?	Yes?	Yes?	Yes?
(E) $K_\sigma = O(q^{2/3})$ for $\rho_q = q\rho_1, 0 < q \leqslant 1$	No	No	No	No	No	Yes
(F) $\lim_{R \to \infty} K_\sigma = \rho_\sigma^{-1/3} R^{-1}$	No	Yes?	No	No	No	No

(D) K_σ expands at a slowly varying density limit ($x_\sigma \to 0$) as[26]

$$\lim_{x_\sigma \to 0} K_\sigma = 3\left(\frac{3}{4\pi}\right)^{1/3}\left(1 + \frac{5}{162(6\pi^2)^{2/3}} x_\sigma^2 + O(x_\sigma^4)\right). \tag{14}$$

Surprisingly, $K_\sigma^{TFW\text{-}\tau_\sigma}$ is solved to give just twice of the gradient expansion coefficient at this limit despite the independent derivation,

$$\lim_{x_\sigma \to 0} K_\sigma^{TFW\text{-}\tau_\sigma} = 3\left(\frac{3}{4\pi}\right)^{1/3}\left(1 + \frac{5}{81(6\pi^2)^{2/3}} x_\sigma^2 + O(x_\sigma^4)\right). \tag{15}$$

Notice that B88 and PBE functionals give coefficients that are close to $5/81(6\pi^2)^{2/3} = 0.004\,063$: $0.004\,514$ in B88 functionals and $0.003\,612$ in PBE functionals. Hence we suspect that the coefficient is incorrectly halved. This remains to be proven. For $K_\sigma^{HF\text{-}\tau_\sigma}$, it should also give the correct gradient expansion coefficient by analogy, because τ_σ^{HF} obviously approaches τ_σ^{TFW} at a slowly varying limit.[27]

(E) For the density $\rho_q = q\rho_1$ ($0 < q \leqslant 1$, ρ_1 is a one-electron density), K_σ is scaled as $O(q^{2/3})$ to become self-interaction free.[28] It is striking that $K_\sigma^{HF\text{-}\tau_\sigma}$ satisfies this condition, because τ_σ^{HF} is scaled exactly as $q\tau_\sigma^{HF}$ for $\rho_q = q\rho_1$. As far as we know, there is still no conventional functional that obeys this condition. The formula of $K_\sigma^{HF\text{-}\tau_\sigma}$ may therefore offer a direction for developing a self-interaction-free exchange functional. By contrast, K_σ^{TFW} is not correctly scaled due to the erroneous q dependency of τ_σ^{TFW} in the constituent τ_σ^{TF}.

(F) To reproduce the asymptotic behavior of the exchange energy density[29] $\epsilon_{x\sigma} \to -1/2R$ for $R \to \infty$, where $\epsilon_{x\sigma}$ is defined as $E_x = \Sigma_\sigma \int \rho_\sigma(\mathbf{R}) \epsilon_{x\sigma}(\mathbf{R}) d^3\mathbf{R}$, K_σ asymptotically approaches $\rho_\sigma^{-1/3} R^{-1}$ at the limit. Near the limit, K_σ^{new} approaches const $\rho_\sigma^{7/3}$ for τ_σ^{TFW} and const $\rho_\sigma^{-1/3}$ for τ_σ^{HF}. The K_σ's of the B88 functional follow the asymptotic behavior for exponentially decaying density, because they contain a term that reduces them to $x_\sigma/(3 \ln x_\sigma)$ at the limit.[29] It may only be possible to obtain the R^{-1} term by incorporating a logarithmic function explicitly in the form of K_σ.

V. CONCLUSIONS

In this paper, we derived a DME-type exchange functional that has a simple form, and contains no adjusted parameter or additional portion for obtaining specific properties. The functional is adapted to any kind of kinetic-energy functional through the kinetic-energy density part.

The exchange energies of H-Ar atoms were calculated by this functional. Consequently, we found that the functional provides accurate exchange energies within a margin of error of a few percent for the Thomas-Fermi-Weizsäcker kinetic-energy density. To ensure the physical validity of the present functional, we then determined which significant and strict conditions for K_σ are violated by the functional and conventional correlation functionals. It was proved that this functional satisfies many of the significant and strict fundamental conditions for providing an exact gradient expansion coefficient and for being self-interaction-free. The advantages of the DME-type exchange functional are as follows.

(1) It keeps a high physical validity. It meets significant and tight fundamental conditions of the exact exchange functional, despite the fact that it was not derived to obey these conditions.

(2) It has a simple form that contains no semiempirical parameter and no adjusted fundamental constant.

(3) Despite the fact that it is a parameter-free functional, it gives accurate exchange energies for atoms within an error on the order of a few percent.

(4) Because it can be corrected for any kind of kinetic-energy functional, the functional is a progressive exchange functional that can be easily updated.

Compared to conventional parametrized exchange functionals, our analytic functional gives slightly less accurate atomic exchange energies. However, it can be refined by replacing the kinetic-energy density τ_σ or upgrading the approximation in the derivation. Actually, we can easily obtain much more accurate results by using a parametrized kinetic-energy density, e.g., $\tau_\sigma = \tau_\sigma^{TF} + x_\sigma^2/36(1 + 0.0024 x_\sigma^2)$, that reproduces τ_σ^{TFW} for a slowly varying density. At the present stage of DFT, there is still no kinetic-energy functional that is either physically valid or applicable to a wide class of problems, as far as we know. We expect that the exchange functional would become a powerful tool in the development of an orbital-free theory with a sophisticated kinetic-energy functional.

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