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REGULAR ARTICLE

Reparameterization of a meta-generalized gradient approximation functional by combining TPSS exchange with τ1 correlation

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Abstract We present a new local meta-GGA exchange-correlation density functional by combining the TPSS meta-GGA exchange and the τ1 meta-GGA correlation functionals. The TPSS meta-GGA exchange-correlation and the τ1 meta-GGA correlation functionals have been implemented in the deMon code. The parameters in the τ1 meta-GGA correlation model are reoptimized in a synchronized way to match the original TPSS meta-GGA exchange counterpart. This reparametrized meta-GGA functional is referred to as "TPSSτ3". The TPSSτ3 and TPSSτ1 meta-GGAs are validated using a test set that consists of covalent molecules, hydrogen-bonded complexes, and van der Waals interactions. The calculated results from TPSSτ1 and TPSSτ3 are analyzed and compared with reliable experimental data and theoretical data, as well as with those from Bmτ1 and TPSS calculations. The τ1 correlation model describes the aromatic compounds better than TPSS. TPSSτ3 yields satisfactory results for the covalent molecules, the hydrogen-bonded complexes, and the van der Waals complexes in the test set compared with TPSS, Bmτ1 and TPSSτ1.

Keywords Density functional theory · Exchange-correlation functional · Meta-generalized gradient approximation · Hydrogen-bonded complexes · van der Waals interactions

1 Introduction

Kohn–Sham (KS) density functional theory (DFT) [1–10] is one of the most active research fields in computational and theoretical chemistry and physics. This is mainly due to the fact that DFT replaces the N-electron wave function by a simpler quantity, the electron density. The conventional ab initio wave function theory (WFT) depends on $4N$ variables (three spatial and one spin variable for each of the N electrons); while DFT, at least in the versions where the functional is independent of orbitals, depends on six variables, three spatial variables for the up spin density, and three spatial variables for the down spin density. The complicated WFT makes a computational treatment very demanding compared to DFT for large molecules. For example, when the atom-centered basis functions and conventional algorithm are employed, the computational cost of DFT calculations scales nominally as N^4, where N is the number of basis functions, although better scaling, including linear schemes may be attained by judicious approximations. In comparison, accurate correlated WFT methods scale as N^7 or higher,

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again with improvements through judicious approximations. Therefore, DFT is more efficient in computation and more widely applied to complex systems than WFT, particularly for large biomolecules of interest.

Within the framework of the Kohn–Sham DFT [2], the ground state energy E of a system of N interacting electrons is expressed as a functional of the electron density n.

$$E = T_s(n) + J(n) + E_{\mathrm{Ne}}(n) + E_{\mathrm{XC}}(n) \tag{1}$$

The first term $T_s(n)$ in Eq. (1) is the kinetic energy of a system of non-interacting electrons of density n. The second term $J(n)$ is the classical Coulomb repulsion energy. The third term $E_{\mathrm{Ne}}(n)$ is the nuclei-electron attraction energy. The last term $E_{\mathrm{XC}}(n)$ is the so-called exchange-correlation energy, and is defined through Eq. (1) as

$$\begin{aligned} E_{\mathrm{XC}}(n) &= [T(n) - T_s(n)] + [E_{\mathrm{ee}}(n) - J(n)] \\ &= T_C(n) + E_{\mathrm{ncl}}(n) \end{aligned} \tag{2}$$

where $T(n)$ is the true kinetic energy of a system of interacting electrons of the density. $E_{\mathrm{ee}}(n)$ is the electrostatic repulsion of the electrons. $E_{\mathrm{ncl}}(n)$ is the non-classical contribution to the electron-electron interaction containing all the effects of self-interaction correction, exchange and Coulomb correlation. n is the total density of all the electrons, which can be given, when the electron spin is considered, by

$$n = n_\uparrow + n_\downarrow \tag{3}$$

The spin density n_σ can be calculated according to the following relation

$$n_\sigma(\mathbf{r}) = \sum_i^{\mathrm{occ}} |\varphi_{i\sigma}(\mathbf{r})|^2 \tag{4}$$

where occ is the number of occupied Kohn–Sham orbitals $\varphi_{i\sigma}$; the occupied KS orbitals $\varphi_{i\sigma}$ are self-consistent solutions of the KS equations.

The kinetic energy $T_s(n_\sigma)$ can be calculated exactly in terms of the occupied KS orbitals $\varphi_{i\sigma}(\mathbf{r})$,

$$T_s = -\frac{1}{2}\sum_{i\sigma}^{\mathrm{occ}} \left\langle \varphi_{i\sigma}(\mathbf{r}) | \nabla^2 | \varphi_{i\sigma}(\mathbf{r}) \right\rangle \tag{5}$$

But the non-interacting kinetic energy T_s in the KS DFT is not equal to the true kinetic energy T of the real, interacting system, $T_s \neq T$, even if the systems share the same density. The difference between the exact kinetic energy of the non-interacting reference system and the true interacting one with the same density is put into the exchange-correlation energy term. Thus, the contributions of the first three terms in Eq. (1) to the total energy of a given system can be obtained from the KS orbitals. The only unknown term of the total energy of Eq. (1) is the exchange-correlation energy functional $E_{\mathrm{XC}}(n)$, which can be developed in practical applications by using different types of approximations. In principle, if the exact exchange-correlation functional were available, the KS DFT could take complete account of all the complex many-body effects at a computational cost comparable with mean-field approximations [3]. Unfortunately, the exact exchange-correlation functional is unknown. Therefore, it is necessary to pursue more accurate approximate exchange-correlation functionals.

Many approximations to the exchange-correlation energy have been developed and tested within the framework of the KS-DFT. DFT methods can be classified in various ways. In this paper we classify the various approaches by the "Jacob's ladder" [11] of size-consistent approximations in terms of the type of ingredients for exchange-correlation functionals they involve. Note that the spin density will be taken into consideration in the following expression of the exchange-correlation energy.

1. Local spin density approximations (LSDA) [12,13] depend only on the spin-up $n_\uparrow(\mathbf{r})$ and spin-down $n_\downarrow(\mathbf{r})$ electron densities. The LSDA exchange-correlation energy can be written as

$$E_{\mathrm{XC}}^{\mathrm{LSDA}}[n_\uparrow, n_\downarrow] = \int n(\mathbf{r})\varepsilon_{\mathrm{XC}}^{\mathrm{unif}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}))d^3\mathbf{r} \tag{6}$$

2. Generalized gradient approximations (GGA) [7,14–16] depend not only on the electron spin densities but also on the electron density gradients $\nabla n_\uparrow(\mathbf{r})$ and $\nabla n_\downarrow(\mathbf{r})$. The GGA exchange-correlation energy can be expressed as

$$\begin{aligned} &E_{\mathrm{XC}}^{\mathrm{GGA}}[n_\uparrow, n_\downarrow] \\ &\quad= \int n(\mathbf{r})\varepsilon_{\mathrm{XC}}^{\mathrm{GGA}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}), \nabla n_\uparrow(\mathbf{r}), \nabla n_\downarrow(\mathbf{r}))d^3\mathbf{r} \end{aligned} \tag{7}$$

3. meta-Generalized gradient approximations (meta-GGA) [4,5,17–24] depend not only on the electron spin densities and the spin density gradients but also on the Laplacians of the electron spin densities $\nabla^2 n_\uparrow(\mathbf{r})$ and $\nabla^2 n_\downarrow(\mathbf{r})$ and /or the electron spin kinetic energy densities $\tau_\uparrow(\mathbf{r})$ and $\tau_\downarrow(\mathbf{r})$.

$$\begin{aligned} &E_{\mathrm{XC}}^{\mathrm{MGGA}}[n_\uparrow, n_\downarrow] \\ &\quad= \int n(\mathbf{r})\varepsilon_{\mathrm{XC}}^{\mathrm{MGGA}}(n_\uparrow(\mathbf{r}), n_\downarrow(\mathbf{r}), \nabla n_\uparrow(\mathbf{r}), \nabla n_\downarrow(\mathbf{r}), \\ &\qquad \nabla^2 n_\uparrow(\mathbf{r}), \nabla^2 n_\downarrow(\mathbf{r}), \tau_\uparrow(\mathbf{r}), \tau_\downarrow(\mathbf{r}))d^3\mathbf{r} \end{aligned} \tag{8}$$

Here the non-interacting kinetic energy density of electrons with spin $\sigma(\sigma = \uparrow, \downarrow)$ is defined, in terms of the occupied KS spin-orbitals $\varphi_{i\sigma}(\mathbf{r})$, as

$$\tau_\sigma(\mathbf{r}) = \sum_i^{\text{occ}} \frac{1}{2}|\nabla\varphi_{i\sigma}(\mathbf{r})|^2 \tag{9}$$

The kinetic energy density is not an explicit functional of the density $n_\sigma(\mathbf{r})$. Note that $\tau_\sigma(\mathbf{r})$, like $n_\sigma(\mathbf{r})$, can be constructed from the KS determinant, and is therefore invariant under unitary transformation of the occupied orbitals. From the expression, Eq. (5), of the kinetic energy operator, it would appear that the non-interacting kinetic energy density should be

$$\tau_\sigma(\mathbf{r}) = -\frac{1}{2}\sum_i^{\text{occ}} \varphi_{i\sigma}^*(\mathbf{r})\nabla^2\varphi_{i\sigma}(\mathbf{r}) \tag{10}$$

The reason that the definition of the kinetic energy density of Eq. (9) is used is the numerical benefit of only having to obtain the first derivative of the basis function with respect to space coordinates. As a matter of fact, both expressions of Eqs. (9) and (10) can integrate to the correct kinetic energy in the case of finite or periodic systems.

In addition, we also mention the so-called hybrid density functionals, which mix a fraction of the nonlocal Hartree–Fock (HF) exchange energy with approximate GGA or meta-GGA exchange functionals [5,10,23,25–30]. The hybrid exchange-correlation energy can be expressed as

$$E_{\text{XC}}^{\text{hybrid}} = aE_X^{\text{HF}} + bE_X^{\text{DFT}} + E_C^{\text{DFT}} \tag{11}$$

Most recently, Grimme [31] proposed a new hybrid density functional with perturbative second-order correlation. The hybrid methods lead in many cases to a considerable improvement over the GGAs and meta-GGAs mainly because a more or less systematic error is compensated by the mixing.

The simplest approximation (LSDA) to E_{xc} has been successful in solid-state electronic structure theory for many years [2,32,33]. The derivation of the LSDA is based on accurate many-body theory of the uniform electron gas. Its success in molecular applications could be in part related to the so-called short-wavelength hypothesis, that is, in any system the interelectronic interaction and correlation at very small length scales behave similarly to a homogeneous electron gas. However, this hypothesis has been proven not to hold in a strict sense. For instance, LSDA contains definite errors, most remarkably the incomplete cancellation of the self-interaction energy and the incorrect asymptotic behavior of the exchange potential for finite systems, which does not allow a correct description of atomic negative ions. The mean absolute deviation (MAD) from experiment for standard enthalpies of formation ($\Delta_f H_{298}^\circ$) for the G3(223) data set at the LSDA/6-311++G(3df,3pd) level of theory is 121.4 kcal/mol [33], which falls far short of chemical accuracy (1 kcal/mol).

Generalized gradient approximations improved the accuracy over LSDA and made density functional theory popular in computational chemistry. GGAs owe their success to a careful analysis of LSDA's shortcomings when molecules are concerned, and finding ways to get rid of spurious side effects associated with truncated gradient expansions of the energy about the LSDA limit. Nonetheless, GGAs do not consistently improve the agreement with experiment, in particular for solids. Moreover, GGAs including the hybrid GGAs neither really improve the description of negative ions nor are able to deal with the van der Waals interactions. For example, Walsh [34] and Hobza [35] have recently shown that the X3LYP [10] functional is not capable of describing the weak interactions in the methane dimer, benzene dimer, or nucleic-base pair stacking, although the functional was designed partly for non-bonded interactions. Walsh also showed that combining HF exchange with the Wilson–Levy correlation (HF-WL) approach [34] can give good predictions for the van der Waals systems, but it would be expected that the approach cannot give satisfactory results for covalent interactions because of the unbalanced exchange and correlation [29]. Lundqvist and Langreth [36,37] have presented a density functional to treat the van der Waals interactions mainly based on a double local density approximation. Kohn [38] and Misquitta [39] used frequency-dependent susceptibilities to include the van der Waals energy. These frequency-dependent methods are computationally very demanding. It becomes clear that it is necessary to develop new exchange-correlation functionals that go beyond GGA.

It is well-known that the van der Waals interactions dominated by "dispersion" play an important role in many areas of science such as molecular recognition, protein folding, stacking of nucleobases and so on. It is especially worth noting that noncovalent interactions including hydrogen-bonded and van der Waals interactions underlie many complex biological functions involving cell–cell recognition, intracellular signaling, and regulation of gene expression. Exploration of the potential applicability of density functional approximations to van der Waals systems is hence of considerable interest. Recently, the so-called meta-GGAs [4–6,17,19–23,30,40,41] have shown to be promising alternatives to the GGA functionals and even to the more sophisticated hybrid DFT schemes [42] due to the additional information of the Laplacian of the electron density and/or the kinetic energy density. Many physicists and chemists [4,20,23,24,43] have argued that the kinetic energy density τ is a natural ingredient of both the exchange and the correlation energy [4–6]. For compatibility, the exchange and correlation should suitably match each other to exhibit a correct long range, asymptotic behavior. For example, the TPSS and TPSSh meta-GGAs have had some notable success in solid state physics and some areas of chemistry. However, they still have difficulties to describe the typically too-long bond lengths and too-small binding energies for van der Waals interactions [44]. The M05-2X [5] hybrid meta-GGA, which was recently developed by Zhao and Truhlar, gives a good description of thermochemistry, thermochemical kinetics, and noncovalent interactions. In addition, M05-2X has a better performance for thermochemical kinetics and noncovalent interactions than M05 [5] because M05-2X is a highly nonlocal density functional with double the amount of the nonlocal HF exchange compared to M05 [45]. It is worth mentioning that M05-2X violates the Lieb-Oxford bound [46]. M05-2X is not able to describe the properties of metals well [5]. The LAP series [17], Bmτ1 [4], and Oτ2 [41] meta-GGAs were developed by Proynov, Salahub et al., in which the correlation functional was derived from an explicit integration over the coupling constant in the adiabatic connection approach. With Bmτ1 [4] and Oτ2 [41] improved results were obtained for the relative energies, activation barriers and equilibrium geometries, in particular for aromatic compounds, systems with weak hydrogen bonds, proton transfer processes and transition-metal carbonyls compared with the LAP series. But the average performance of the Bmτ1, Oτ1, and Oτ2 schemes for typical covalent molecules remains slightly inferior to the hybrid schemes such as B3LYP [25]. In addition, these DFT methods didn't include any van der Waals interactions in the training sets and test sets. Many researchers have thought that the nonlocal HF exchange plays an important role in describing the long-range behavior of weakly bound systems. Indeed, the hybrid methods [5,29] obtain encouraging results for thermochemistry, thermochemical kinetics, and noncovalent interactions because of systematic compensation of errors achieved by the mixing, at the expense of some increase of the computational cost. A local exchange-correlation functional depends on the density, its Taylor series, or the orbitals at a point in space; while nonlocal HF exchange explicitly depends on the Hartree–Fock orbitals. However, the mixture of a local exchange-correlation functional with a nonlocal HF exchange does bring some negative side effects that are inherent to the HF ab initio level itself [47]. One should keep in mind that the charge density in the KS approach is by definition the exact density of the real ground state, while the HF orbitals give the HF ground state wave function, whose square certainly does not integrate to the correct ground state density. This is one of the reasons that none of the existing correlation functional so far has been capable of matching to the nonlocal HF exchange alone very well, although the HF-WL [34] density functional obtained encouraging results for the van der Waals complexes. Taking into account the economy of the calculations and applications to large systems, we prefer to develop a local density functional without a fraction of nonlocal HF exchange. Thus, it is very interesting to investigate if the τ1 meta-GGA correlation model can systemically describe strongly bonded systems, hydrogen-bonded complexes, and van der Waals interactions by combining other meta-GGA exchange functionals without mixing the nonlocal HF exchange.

The exchange component of the total KS-DFT energy and potential is usually larger than the correlation component. Thus, the performance of the exchange-correlation functional depends mainly on the choice of the exchange counterpart. Following the nonempirical philosophy, the TPSS [6] meta-GGA exchange functional was constructed based on physical constraints to yield accurate energies under uniform coordinate scaling to the low-density or strong-interaction limit. The enhancement factor F_X for the TPSS meta-GGA exchange part is more reasonable than those of the B88 [7] GGA and the OPTX [48] GGA exchanges on the basis of the physical constraints [6]. In order to clearly differentiate them, the enhancement factors of the B88 GGA, OPTX GGA, and TPSS meta-GGA exchange as a function of the reduced gradient s at the iso-orbital limit are plotted in Fig. 1. The enhancement factor of the B88 GGA always goes up as s increases, which seriously violates the Lieb-Oxford bound [46]. When $s \to \infty$, $F_X^{\mathrm{OPTX}} \to 2.960$, $F_X^{\mathrm{TPSS}} \to 1.804$. It is clear that the enhancement factor of the TPSS meta-GGA is closer to the Lieb–Oxford bound (1.679) than that of the OPTX GGA. We also found that the value of $a_0 = 10\%$ in the TPSSh [44] hybrid meta-GGA is smaller than for a typical GGA hybrid (about 20%) [47]. This fact suggests that the TPSS meta-GGA is a better approximate exchange functional than the other GGAs. The TPSS meta-GGA is considered

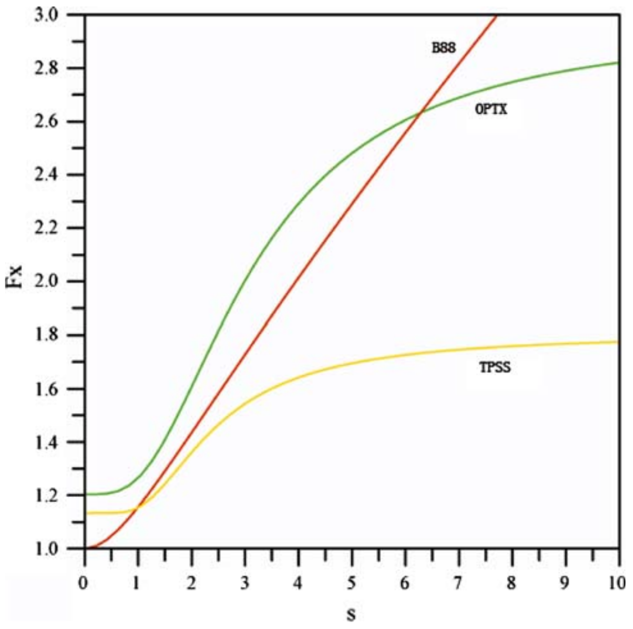

Fig. 1 The exchange enhancement factors F_X for B88 GGA, OPTX GGA, and TPSS meta-GGA as a function of the reduced density gradient s. The curve of the TPSS exchange enhancement factor is drawn with the iso-orbital limit [6]

to be a good platform to develop more accurate approximate exchange-correlation functionals [6].

Interatomic interactions can be classified into covalent bonds, hydrogen-bonds, and van der Waals interactions according to their strength and bond length. Covalent bonds, which occur when atoms share electrons, are the strongest bonds. Covalent bond lengths range from 1.0 to 1.6 Å, giving a typical binding energy of ∼80 kcal/mol. However, this bond energy can vary from ∼50 to ∼110 kcal/mol depending on the elements involved and on the types of bond. Hydrogen bonds occur when a hydrogen atom is shared between two molecules, with bond lengths of ∼2.5 Å and strengths ∼5 kcal/mol. Hydrogen bonds often have a decisive influence on the chemical properties of substances. Hydrogen bonds stabilize the secondary and tertiary structures of proteins and are thought to play a major role in substrate recognition, binding and enzymatic catalysis. At long distances van der Waals complexes are held together by dispersion forces (or London forces). The London dispersion force is a long-range attractive interaction that acts between separated molecules even in the absence of charge or permanent electric moments. In the asymptotic limit, van der Waals attraction decays with the inverse sixth power of the intermolecular distance (R^{-6}). The dispersion interaction should be described by the correlation functional, since it is purely a dynamical correlation effect. Of course, the exchange functionals need to be improved because the long-range exchange also plays some role in the dispersion interaction. The distance between monomers in van der Waals complex is about 3.5 Å, generally with interaction energy of about 1 kcal/mol.

At these distances the electron clouds overlap and, in perturbational approaches, corrections or damping factors have to be applied. Alternatively, in super-molecular approaches such as those used in this work, one can view the "damped dispersion" interactions as being simply a part of the correlation energy. Parameters in the exchange-correlation functional can then be adjusted to hopefully attain an adequate representation of the interaction for distances around 3.5–5 Å. Most of the existing GGAs, B3LYP [26], PBE [16], HTCH407, [8] etc., can describe covalent molecules and hydrogen-bonded complexes. Unfortunately, they are not able to describe van der Waals systems. In order to overcome the deficiency of these GGAs, an empirical van der Waals correction method [9,49] was adopted by adding explicit R^{-6} terms to density functionals. In such methods, one needs to develop different parameters for different atoms and in some cases even for different hybridization states [49]. The so-called meta-GGAs [4,5,24,29,30,44,50,51] obtained encouraging results for van der Waals systems, which can more or less describe the nonlocal properties for weak interactions. Particularly, the hybrid PWB6K [29], M05 [5], M05-2X [5] meta-GGAs, and the local M06-L [30] meta-GGA developed by Zhao, Truhlar et al. obtained good descriptions for thermochemistry, thermochemical kinetics, and noncovalent interactions. It is very encouraging that the conclusions drawn from the local M06-L functional, which appeared in print after the present manuscript was submitted, go against the widespread belief that local functionals are not capable of improving on the broad average accuracy of the best current hybrid functionals, for example, B3LYP. As mentioned above, Grimme proposed a semiempirical exchange-correlation functional, called B2-PLYP [31]. The virtual orbital-dependent functional contains only two global parameters that describe the mixture of HF and Becke88 [7] GGA exchange and of the second-order perturbation theory (MP2) and LYP [15] GGA correlation, and employs the KS orbital and eigenvalues as input for a standard MP2 perturbation correction [52,53]. The B2-PLYP functional represents a successful step along a not quite well-explored direction. The accuracy of B2-PLYP for many important parts of chemistry is satisfactory. However, B2-PLYP still has difficulties to describe the dispersion-dominated complexes because the GGA parts are purely repulsive and the attractive MP2 contribution is too small. When expensive calculations are affordable, B2-PLYP can be regarded as a general purpose density functional for molecules.

The purpose of the present work is to examine whether combining the original TPSS meta-GGA exchange with a reparametrized τ1 meta-GGA correlation model could give a good description for covalent molecules, hydrogen-bonded complexes, and van der Waals interaction complexes in a semiempirical fashion.

2 Description and implementation of density functionals

2.1 The TPSS meta-GGA exchange functional

We give only a brief description of the TPSS meta-GGA exchange and the τ1 meta-GGA correlation functionals. Full details may be found in the original TPSS [6,24] and τ1 [4] papers. The TPSS meta-GGA for exchange was developed from the PBE [16] GGA exchange energy, in which the enhancement factor F_X depends on the reduced density gradient s. Additionally, exact constraints for small s were imposed. Small s can occur in the three different situations: (a) A nearly uniform density with sinusoidal static oscillations of small amplitude and arbitrary wave vector k. (b) A static density that varies slowly over space, and (c) near the nucleus of an atom, where the PBE GGA exchange potential for the H atom has a spurious divergence that TPSS has not [27], and near the extremum of the density in a covalent bond. The TPSS exchange functional was constructed to take into account all three of the situations (a), (b) and (c). The exchange energy for a spin-polarized system may be evaluated from the exchange functional for a spin-unpolarized system using the spin-scaling relation [54]:

$$E_X(n_\uparrow, n_\downarrow) = \frac{1}{2}E(2n_\uparrow) + \frac{1}{2}E(2n_\downarrow) \tag{12}$$

Thus, the TPSS meta-GGA exchange energy for the spin-unpolarized (or spin-compensated,$n_\uparrow = n_\downarrow$) system can be simply expressed by

$$E_{X\sigma}^{\mathrm{TPSS}}(n_\sigma) = \int n_\sigma \varepsilon_{X\sigma}^{\mathrm{unif}}(n_\sigma) F_{X\sigma}(p_\sigma, z_\sigma) d^3\mathbf{r} \tag{13}$$

$$\varepsilon_{X\sigma}^{\mathrm{unif}}(n_\sigma) = -\frac{3}{4\pi}(3\pi^2 n_\sigma)^{1/3} = -\frac{3}{4\pi}k_F \tag{14}$$

$$k_F = (3\pi^2 n_\sigma)^{1/3} \tag{15}$$

where $\varepsilon_{X\sigma}^{\mathrm{unif}}(n_\sigma)$ is the exchange energy per particle of a spin-unpolarized uniform electron gas [55]. k_F is the local Fermi wave vector [1]. p_σ and z_σ are two dimensionless inhomogeneity parameters of the enhancement factor, which are given by

$$p_\sigma = \left(\frac{|\nabla n_\sigma|}{2k_F n_\sigma}\right)^2 = s_\sigma^2, \tag{16}$$

$$z_\sigma = \frac{\tau_\sigma^W}{\tau_\sigma} \le 1 \tag{17}$$

$$\tau_\sigma^W = \frac{1}{8}\frac{|\nabla n_\sigma|^2}{n_\sigma} \tag{18}$$

where τ_σ^W is the von Weizsäcker spin kinetic energy density; [56] s is the reduced spin density gradient.

The enhancement factor of the TPSS meta-GGA exchange functional satisfies the Lieb-Oxford bound [46] and recovers the large-p behavior of the PBE enhancement factor, which is expressed by

$$F_{X\sigma} = 1 + \kappa - \frac{\kappa}{1 + x_\sigma/\kappa} \tag{19}$$

$$\begin{aligned} x_\sigma = \Bigg\{ & \left[\frac{10}{81} + c\frac{z_\sigma^2}{(1+z_\sigma^2)^2}\right] p_\sigma + \frac{146}{2025}\tilde{q}_{b\sigma}^2 \\ & - \frac{73}{405}\tilde{q}_{b\sigma}\sqrt{\frac{1}{2}\left(\frac{3}{5}z_\sigma\right)^2 + \frac{1}{2}p_\sigma^2} + \frac{1}{\kappa}\left(\frac{10}{81}\right)^2 p_\sigma^2 \\ & + 2\sqrt{e}\frac{10}{81}\left(\frac{3}{5}z_\sigma\right)^2 + e\mu p_\sigma^3 \Bigg\} \Big/ (1+\sqrt{e}p_\sigma)^2 \end{aligned} \tag{20}$$

$$\tilde{q}_{b\sigma} = (9/20)(\alpha_\sigma - 1)/[1 + b\alpha_\sigma(\alpha_\sigma - 1)]^{1/2} + 2p_\sigma/3 \tag{21}$$

$$\alpha_\sigma = \frac{\tau_\sigma - \tau_\sigma^W}{\tau_\sigma^{\mathrm{unif}}} = (5p_\sigma/3)(z_\sigma^{-1} - 1) \ge 0 \tag{22}$$

$$\tau_\sigma^{\mathrm{unif}} = \frac{3}{10}(3\pi^2)^{2/3} n_\sigma^{5/3} \tag{23}$$

where $\tau_\sigma^{\mathrm{unif}}$ is the Thomas–Fermi spin kinetic energy density [57,58]. The constants in Eqs. (19–21) are $\kappa = 0.840$, $\mu = 0.21951$, $c = 1.59096$, $e = 1.537$, and $b = 0.40$.

2.2 The τ1 meta-GGA correlation functional

A formally rigorous procedure of deriving the correlation energy in the KS DFT is the adiabatic connection [1], that is, a virtual process is considered of gradually turning on the electron interaction adiabatically, i.e. without exciting the system and keeping the electron density equal to the exact density of the real interacting system along this process. The application of the Hellmann–Feynman theorem leads to the adiabatic connection formula (ACF) [59–61]:

$$E_C(n) = \tilde{E}_C(n)^{\lambda=1} + T_C(n) \tag{24}$$

where $\tilde{E}_C(n)^{\lambda=1}$ is the "physical" correlation energy; $T_C(n)$ is the correlation contribution to the kinetic energy, which is usually a small but not negligible remainder to the SCF kinetic energy obtained via the KS determinant. The coupling strength parameter λ connects adiabatically the ground state of the KS non-interacting reference system (at $\lambda = 0$ with the ground state of the interacting N-electron system (at $\lambda = 1$).

The correlation energy can be further divided into two parts: parallel-spin and antiparallel-spin components.

$$E_C = E_C^{\uparrow\downarrow} + E_C^{\sigma\sigma} \tag{25}$$

$$E_C^{\sigma\sigma} = E_C^{\uparrow\uparrow} + E_C^{\downarrow\downarrow} \tag{26}$$

By resolving the corresponding λ- and spin-dependent pair correlation formula (PCF) [60,61], the correlation energy density for the antiparallel-spin case is obtained:

$$\varepsilon_C^{\uparrow\downarrow} = \frac{n_\uparrow n_\downarrow}{n} Q^{\uparrow\downarrow}(k^{\uparrow\downarrow}) + \frac{B_{\uparrow\downarrow}^2}{n} Q_2^{\uparrow\downarrow}(k^{\uparrow\downarrow}) \tag{27}$$

where

$$\begin{aligned} B_{\uparrow\downarrow}^2 \approx \beta_2 \Bigg[& \frac{1}{12}(n_\uparrow \nabla^2 n_\downarrow + n_\downarrow \nabla^2 n_\uparrow) \\ & - \frac{1}{6}(\nabla n_\uparrow \nabla n_\downarrow) \Bigg] e^{(-c/n^{1/3})} \end{aligned} \tag{28}$$

$$Q^{\uparrow\downarrow}(k) = -\frac{b_1}{1 + b_2 k} + \frac{b_3}{k}\ln\left(\frac{b_4 + k}{k}\right) + \frac{b_5}{k} - \frac{b_6}{k^2} \tag{29}$$

$$Q_2^{\uparrow\downarrow}(k) = -\frac{c_1}{k^2(1 + c_2 k)} - \frac{c_3}{k^3}\ln\left(\frac{c_4 + k}{k}\right) + \frac{c_5}{k^3} + \frac{c_6}{k^4} \tag{30}$$

$$k_\sigma^2 \approx \alpha_e^2 \frac{2}{3}\frac{t_\sigma}{n_\sigma} \tag{31}$$

$$k_{\uparrow\downarrow} = \frac{2k_\uparrow k_\downarrow}{k_\uparrow + k_\downarrow} \tag{32}$$

$$t_\sigma = \tau_\sigma - \frac{1}{8}\nabla^2 n_\sigma \tag{33}$$

where k_σ is the parallel-spin correlation wave vector. $k_{\uparrow\downarrow}$ is the antiparallel-spin correlation wave vector, which is determined using the approximation of Becke [62]. The quantity

t_σ in Eq. (33) is defined as the occupied KS spin kinetic energy density in the original τ1 model [4]. Here, we rewrite this term in order to be consistent with the definition of the commonly used kinetic energy density of Eq. (10) by Perdew et al. [20] It is worth noting that t_σ is a linear combination of the spin kinetic energy density and the Laplacian of the electron spin density, and is different from that $[D_\sigma = 2(\tau_\sigma - \tau_\sigma^W)]$ defined by Becke [63]. b_i and c_i are coefficients resulting from the analytic integration over λ. $b_1 = 2.763169$; $b_2 = 1.757515$; $b_3 = 1.741397$; $b_4 = 0.568985$; $b_5 = 1.572202$; $b_6 = 1.885389$; $c_1 = 0.583090$; $c_2 = 1.757515$; $c_3 = 4.377624$; $c_4 = 0.568985$; $c_5 = 0.331770$; $c_6 = 2.302031$.

Using the above similar derivation, the correlation energy for the parallel-spin part is expressed as

$$\varepsilon_C^{\sigma\sigma} = \frac{1}{2}\left(1 - \frac{1}{N_\sigma}\right)\frac{n_\sigma^2}{n}[Q^{\sigma\sigma}(k_\sigma) + B_{\sigma\sigma}^2 Q_2^{\sigma\sigma}(k_\sigma)] \qquad (34)$$

where

$$Q^{\sigma\sigma}(k_\sigma) \approx C_p Q^{\uparrow\downarrow}(k_\sigma) \qquad (35)$$

$$B_{\sigma\sigma}^2 \approx \frac{\gamma_2}{n_\sigma}\left[\tau_\sigma - \frac{1}{4}\frac{|\nabla n_\sigma|^2}{n_\sigma}\right]\exp(-c/n^{1/3}) \qquad (36)$$

$$Q_2^{\sigma\sigma}(k_\sigma) \approx C_p Q_2^{\uparrow\downarrow}(k_\sigma) \qquad (37)$$

where N_σ is the total number of electrons with spin σ and the term, $(1 - 1/N_\sigma)$, is a correction of Fermi-Amaldi type [1,19], which guarantees that the parallel-spin correlation energy is zero when there is only one electron per spin direction for the given system. C_p is an empirical factor ranging between 0 and 1, introduced to monitor the relative share of parallel-spin correlation to the total correlation energy. Note that the form of Eq. (36) is not the same as that of Eq. (31) in the original τ1 model [4], but the two equations are essentially the same, the differences reflecting the different definition of the kinetic energy density used in the present paper.

2.3 Implementation of meta-GGAs

The PKZB [20] and TPSS [6,24] meta-GGAs depend not only on the electron density, the density gradient but also on the kinetic energy density. To perform a KS calculation in a fully self-consistent way, the exchange-correlation potential $V_{\mathrm{XC}}(\mathbf{r}) = \frac{\delta E_{\mathrm{XC}}}{\delta n(\mathbf{r})}$ has to be calculated. From the definition of the exchange-correlation potential, V_{XC} appears to be a local potential in the KS single-particle Hamiltonian. However, the additional term, the kinetic energy density (τ), which is introduced by the meta-GGA exchange-correlation functionals, is not known as an explicit function of the electron density. Thus, $\frac{\delta E_{\mathrm{XC}}^{\mathrm{MGGA}}}{\delta n(\mathbf{r})}$ cannot directly be derived since this requires the knowledge of the exact relation between the kinetic energy density and the electron density. The KS exchange-correlation energy and potential can in principle be calculated exactly as a functional of the KS orbitals by means of the optimized effective potential (OEP) [49,64–68] method.

However, OEP is a rather difficult and costly procedure to implement in practice. The determination of the OEP can be avoided by departing slightly from the true KS scheme and minimizing the energy functional with respect to the KS orbitals. In our implementation of meta-GGA in the deMon program, we therefore follow Handy et al.'s method [69, 70] and evaluate the derivative of the meta-GGA exchange-correlation energy with respect to the Kohn–Sham orbitals instead of the electron density in the KS single-particle equation. In addition, the second derivatives of the KS orbitals have to be calculated according to the conventional self-consistent field procedure. In order to avoid computational difficulties, we employ efficient formulas for computing matrix elements of the exchange-correlation potential in the finite basis sets developed by Pople et al. [71] and Neumann et al. [70] Analytical energy gradients for geometry optimizations are available for the PKZB and TPSS meta-GGAs in the deMon2k suite [72].

For the τ1 meta-GGA correlation functional, the τ1 meta-GGA correlation energy and potential are implemented in a non-self-consistent way in the present work. The ML2 [73] gradientless form of the potential is used instead of the τ1 meta-GGA correlation potential. The main reasons for excluding the nonlocal terms from the τ1 meta-GGA correlation potential are the following. (1) The numerical implementation of Eqs. (31–33) is quite demanding and requires a careful handling of singularities [4]. (2) The reduced Laplacian of the electron density diverges at the nuclei, which suffers from numerical instabilities with respect to small density changes [33,74]. We will implement the τ1 meta-GGA correlation functional in a fully self-consistent method in the future.

3 The TPSSτ3 training set and test set

The performance of an exchange-correlation functional mainly depends on the functional form [5,23,28]. When the functional form is inadequate, high accuracy cannot be obtained even by fitting a diverse set of data. For the semiempirical approach to the development of DFT, once the exchange-correlation form is determined, the choice of training set is helpful in parametrizing density functional. In principle, a balanced training set for the parametrization of density functionals should contain a variety of molecules from strongly bonded complexes to weakly bonded complexes. In addition, the contribution of different interactions should correspond to their relative strength and abundance in nature. At this stage, the parametrization and assessment of density

Table 1 Molecules in the TPSSτ3 test set

1. Atomization energies:
   (a) Diatomic molecules:
      $H_2, N_2, F_2, O_2, S_2, P_2, Cl_2$, HF, CO, NO, PN, CN, NH, CS, CH, OH, HCl, SiO, NaCl, NaF
   (b) Polyatomic molecules:
      HCN, $H_2O, H_2S, CO_2, NH_3, PH_3, N_2O, H_2O_2, CH_4, C_2H_2, C_2H_4, C_2H_6, H_2CO$, CH_3OH, C_6H_6, 1,3-butadiene (C_4H_6), pyrrole (C_4H_5N), pyridine (C_5H_5N)
2. Hydrogen-bonded complexes:
   $(H_2O)_2, (NH_3)_2$
3. van der Waals complexes:
   $(CH_4)_2, (C_2H_2)_2$

functionals depend on the type and size of the training set and the test set used, and also on the basis set used for the calculations [4,5,8,23,75]. For example, BMK [28] uses the same functional form as τ-HCTHh [23], but is was reparametrized against a data set for thermochemistry and kinetics. BMK performs equally well for thermochemistry and kinetics. However, BMK's performance for noncovalent interactions is inferior to PWB6K [29], M05 [5], and M05-2X [5]. An ideal parametrized density functional should describe various properties for molecules of interest, such as covalent molecules, hydrogen-bonded complexes, and van der Waals interactions. For instance, Handy et al. [8] used a large training (fitting) set including 407 molecules to determine the parameters in the HCTH/407 density functional. A hindrance to using these data sets for such purposes is that calculations on hundreds of structures are required for comparison. This is both computationally expensive and technically cumbersome. In fact, HCTH/407 did not give good results for van der Waals interactions that were not included in the large training set. To overcome the difficulties, Truhlar et al. [76] proposed a small training set that can be a representative of large data sets. They used a small training set to determine the parameters of the PW6B95 [29], PWB6K [29], M05 [5], and M05-2X [5] density functionals. In particular, with the M05-2X hybrid meta-GGA they obtained satisfying results for van der Waals interactions. The strategy of selecting a small training set has been adopted to develop exchange-correlation functionals by Proynov et al. [4,17–19,73] Note that after our present work was submitted, Zhao and Truhlar reported a new local meta-GGA density functional, called M06-L [30], which contains 34 parameters. A large training set that includes 314 data was used during the parametrization of M06-L.

Our present training set consists of the following species: The correlation energies of C, N, O and F atoms, the atomization energies of N_2, F_2, O_2, HF, CN, $H_2O, CH_4, C_2H_4, C_2H_2, NH_3, C_6H_6$, the interaction energies of the water dimer $(H_2O)_2$ and the ethene dimer $(C_2H_2)_2$, for which reliable experimental and theoretical data are available. The present training set is similar to that used in Refs. [4,19,41]. Furthermore, C_2H_2 has been added. Besides, a complex with van der Waals interaction (ethene dimer) is also added to represent more weakly bound systems. $(C_2H_2)_2$ is stabilized by π–π interactions with a moderately strong interaction energy for van der Waals interactions. Thus, it is regarded as a representative of weak interactions.

Besides TPSSτ3, we report the results calculated by TPSSτ1. TPSSτ1 combines the TPSS exchange and the original τ1 correlation in which the parameters are not reoptimized; while the parameters in the TPSSτ3 are optimized against our present training set. In order to validate the accuracy of TPSSτ1 and TPSSτ3 for thermochemistry, we use a medium-sized test set of molecules for which there are quite accurate experimental data and high level ab initio calculations available [4,75,77]. The water dimer $(H_2O)_2$, the ammonia dimer $(NH_3)_2$, the methane dimer $(CH_4)_2$, and the ethene dimer $(C_2H_2)_2$ are included in the test set to assess the accuracy of hydrogen bonded complexes and van der Waals complexes, respectively. The test set for TPSSτ1 and TPSSτ3 is listed in Table 1.

4 Computational details

The TPSS meta-GGA exchange-correlation and the τ1 correlation functionals have been implemented in the deMon2k package [72]. Gaussian basis functions and Gaussian fit functions for the variational approximation of the Coulomb potential are used in the deMon2k package [32]. All calculations used the spin-restricted formalism for closed-shell systems and the spin-unrestricted formalism for open-shell systems. All calculations were carried out with this software. For the molecules in the TPSSτ3 training set and test set, the Ahlrichs basis set A-pVTZ [78] and the GEN-A2 auxiliary

Table 2 Correlation energies of atoms, $-E_C$, in hartrees

Atom	TPSSτ3EC[a]	TPSSτ3AE[b]	Bmτ1[c]	Oτ2[d]	TPSSτ1	TPSSτ3	$-E_C$(I)[e]	$-E_C$(II)[f]
He	0.042	0.042	0.048	0.048	0.049	0.050	0.042	0.042
Be	0.094	0.080	0.095	0.094	0.096	0.097	0.094	0.094
B	0.125	0.104	0.124	0.123	0.124	0.126	0.125	0.125
C	0.157	0.133	0.156	0.155	0.156	0.158	0.156	0.157
N	0.188	0.164	0.191	0.190	0.191	0.193	0.188	0.189
O	0.253	0.219	0.254	0.253	0.254	0.258	0.258	0.258
F	0.323	0.283	0.326	0.325	0.327	0.332	0.325	0.325
Ne	0.394	0.354	0.405	0.403	0.406	0.411	0.390	0.388
Na	0.432	0.387	0.443	0.441	0.443	0.451	0.396	0.412
Mg	0.480	0.432	0.493	0.491	0.493	0.502	0.438	0.466
Al	0.524	0.471	0.537	0.536	0.537	0.546	0.470	0.507
Si	0.568	0.513	0.583	0.583	0.583	0.593	0.505	0.554
P	0.614	0.556	0.632	0.632	0.632	0.641	0.504	0.615
S	0.685	0.620	0.703	0.704	0.704	0.715	0.605	0.692
Cl	0.758	0.688	0.780	0.781	0.781	0.792	0.666	0.789
Ar	0.833	0.760	0.860	0.861	0.861	0.873	0.722	0.862
MAD(I)	0.038	0.022	0.047	0.045	0.045	0.053		
MAD(II)	0.009	0.042	0.012	0.011	0.012	0.016		
MAPD(I)	6.94%	7.70%	9.71%	9.63%	9.99%	11.36%		
MAPD(II)	1.68%	10.59%	3.40%	3.28%	3.64%	4.68%		

[a] The correlation energies are calculated using TPSSτ1EC with basis set A-PVTZ. The TPSSτ1EC is designed to reproduce as much as possible the E_C(II) data set

[b] The correlation energies are calculated using TPSSτ1AE with basis set A-PVTZ. The TPSSτ1AE is designed to reproduce as much as possible the experimentally derived total energies of atoms from He to Ar

[c] Ref. [4]; [d] Ref. [41]; [e] Ref. [96]; [f] Ref. [97]

Table 3 Total energies of atoms

Atom	$-E$(TPSSτ3EC)	$-E$(TPSSτ3AE)	$-E$(TPSSτ1)	$-E$(TPSSτ3)	$-E$(exact)[a]
He	2.9071	2.9089	2.9138	2.9149	2.9037
Be	14.6771	14.6586	14.6781	14.6798	14.6674
B	24.6751	24.6477	24.6735	24.6754	24.6539
C	37.8712	37.8467	37.8702	37.8724	37.8450
N	54.6165	54.5813	54.6190	54.6214	54.5892
O	75.1167	75.0673	75.1174	75.1208	75.0673
F	99.7984	99.7393	99.8024	99.8069	99.7339
Ne	129.0138	128.9475	129.0244	129.0302	128.9376
Na	162.3462	162.2731	162.3569	162.3636	162.2546
Mg	200.1468	200.0666	200.1593	200.1668	200.0530
Al	242.4540	242.3613	242.4665	242.4747	242.3460
Si	289.4704	289.3691	289.4838	289.4927	289.3590
P	341.3701	341.2611	341.3858	341.3952	341.2590
S	398.2311	398.1078	398.2477	398.2584	398.1100
Cl	460.2797	460.1433	460.2997	460.3116	460.1480
Ar	527.6790	527.5337	527.7041	527.7173	527.5400
MAD	0.0741	0.0074	0.0834	0.0896	
MAPD	0.06%	0.02%	0.07%	0.08%	

All values are hartrees

[a] Ref. [96]

Table 4 The deviations of atomization energies (kcal/mol) of diatomic molecules from experiment at experimental geometries

Molecule	TPSSτ3EC	TPSSτ3AE	Bmτ1[a]	TPSS	TPSSτ1	TPSSτ3	Expt.[b]
H_2	2.53	2.65	3.69	6.12	5.98	6.54	109.54
N_2	−0.33	−8.03	1.38	−5.00	−0.35	0.30	228.52
F_2	6.80	8.24	9.69	7.87	9.19	8.91	38.51
O_2	−2.93	−0.77	7.15	4.98	0.97	0.99	120.60
S_2	−7.26	−3.36	−2.31	2.31	−2.67	−3.03	101.69
P_2	−7.73	−8.39	−5.53	−6.09	−4.06	−3.97	117.14
Cl_2	−6.56	−2.84	−3.69	−0.44	−2.82	−3.36	57.88
HF	−6.94	−6.10	0.92	−2.92	−3.60	−3.27	140.90
CO	−6.41	−7.60	−0.46	−5.88	−3.39	−3.13	259.19
NO	−0.67	−4.09	0.92	0.67	0.76	1.10	152.89
PN	−2.94	−7.63	2.08	−5.57	−1.63	−1.24	143.43
CN	−3.14	−8.20	0.00	0.18	−3.31	−3.07	181.02
NH	5.81	−0.59	2.77	5.61	3.85	4.12	83.48
CS	−7.77	−8.81	−3.46	−4.07	−5.41	−5.37	171.34
CH	6.55	0.83	2.31	4.15	5.16	5.40	83.71
OH	−1.73	−3.92	3.23	−0.03	−0.48	−0.14	106.31
HCl	−2.39	−3.11	−0.69	1.43	−0.39	−0.17	106.31
SiO	−11.70	−10.91	−3.69	−11.67	−7.83	−7.79	192.32
NaCl	−4.78	−6.03	−6.23	−4.11	−4.12	−4.66	98.01
NaF	−6.56	−7.58	−2.08	−6.77	−5.45	−5.82	114.84
MD	−2.91	−4.31	0.03	−0.96	−0.98	−0.88	
MAD	5.08	5.48	3.11	4.29	3.57	3.62	

MD is the mean deviation, namely, the signed mean deviation, MAD denotes the mean absolute deviation of atomization energy from experiment

[a] The atomization energies are calculated using basis set TZVP (Ref. [4])

[b] The experimental atomization with zero-point-energy removed (Ref. [21])

basis set [32,79–81] are used. For the covalent molecules, the atomization energies are computed at the experimental geometries [82–84], and the experimental atomization energies excluding zero point energies are taken from Refs. [4,85,86] as the reference atomization energies. Therefore, they can be directly compared with the differences between the pure electronic energies. The CCSD(T)/cc-pVQZ geometries of $(H_2O)_2$, $(NH_3)_2$, and $(CH_4)_2$ are adopted and the reference interaction energies are taken from high level ab initio calculations [77]. Here, CCSD(T) [87] denotes coupled cluster calculation with single and double excitations and quasiperturbative contribution of connected triple excitations. The CCSD(T) scheme is considered as one of the most accurate single-reference methods. cc-pVQZ [88] is a correlation consistent polarized valence quadruple-zeta basis set.

For the van der Waals interaction complex $(C_2H_2)_2$, the MC-QCISD/3 [89] geometry is used and the reference interaction energy is taken from Ref. [75] MC-QCISD is the multicoefficient QCISD method [89,90] developed by Truhlar et al. For the hydrogen-bonded complexes and the van der Waals interactions, the counterpoise (CP) [91,92] correction for the basis set superposition error (BSSE) is adopted.

5 Optimization of the parameters

Now we turn to the optimization strategy. In light of the merits of the TPSS exchange mentioned by Perdew et al. [6] and discussed in Sect. 1, we keep the original parameters of the TPSS meta-GGA exchange in the present study. Thus, only the parameters in the τ1 meta-GGA correlation functional model are optimized. As mentioned in the references [17,19], calibrating a correlation functional with respect to conventional atomic correlation energies or total atomic energies alone does not guarantee optimal results for atomization energies and interaction energies for hydrogen-bonded complexes and van der Waals interactions. To illustrate these points, we designed two special parametrizations of the TPSS meta-GGA exchange and the τ1 meta-GGA correlation functionals (denoted as TPSSτ3EC and TPSSτ3AE) by fitting the experimentally derived correlation energies and total energies of atoms from He to Ar except for Li, respectively. The results for the tested TPSSτ3EC and TPSSτ3AE methods are tabulated in Tables 2, 3, 4, and 5. We can see from Table 2 that the mean absolute deviation (MAD(II)) and the mean absolute percent deviation (MAPD(II)) from TPSSτ3EC are 0.009

Table 5 The deviations of atomization energies (kcal/mol) of polyatomic molecules from experiment at experimental geometries

Molecule	TPSSτ3EC	TPSSτ3AE	Bmτ1[a]	TPSS	TPSSτ1	TPSSτ3	Expt.[b]
HCN	−0.13	−8.33	3.69	−0.42	0.57	1.09	312.69
H_2O	−10.34	−12.12	2.54	−4.91	−6.02	−5.37	232.21
H_2S	−0.10	−4.34	0.00	3.95	1.98	2.42	182.40
CO_2	−9.08	−7.17	6.92	−1.95	−1.63	−1.46	389.02
NH_3	−1.86	−11.39	5.30	1.81	−0.43	0.45	297.47
PH_3	2.91	−7.80	2.08	3.08	2.87	3.49	241.67
N_2O	−0.53	−4.21	12.45	5.39	4.03	4.55	270.49
H_2O_2	−8.80	−11.03	8.53	−2.32	−3.11	−2.65	268.65
CH_4	4.87	−7.53	4.84	10.21	5.37	6.08	419.23
C_2H_4	3.64	−12.19	4.38	9.93	3.88	4.45	562.66
C_2H_2	−3.85	−12.71	1.38	0.53	−2.46	−2.06	405.39
C_2H_6	4.82	−16.79	1.15	15.00	4.60	5.34	710.71
H_2CO	1.86	−5.20	6.23	4.95	4.57	5.01	373.57
CH_3OH	−3.13	−14.93	4.38	4.65	−0.14	0.48	511.93
C_6H_6	−7.33	−36.13	−4.61	21.40	−3.46	−3.27	1366.07
C_4H_6(1,3-butadiene)	4.66	−22.76	2.54	18.37	4.68	5.11	1011.18
C_4H_5N(pyrrole)	−11.57	−33.57	−3.00	15.75	−6.34	−5.86	1070.45
C_5H_5N(pyridine)	−6.37	−33.48	−1.15	18.84	−2.43	−2.13	1236.48
MD	−2.24	−14.54	3.20	6.90	0.36	0.87	
MD (from Tables 4, 5)[c]	−2.59	−9.16	1.68	2.76	−0.34	−0.05	
MAD	4.77	14.54	4.18	7.97	3.25	3.40	
MAD (from Tables 4, 5)[c]	4.93	9.97	3.62	6.04	3.42	3.52	

[a] The atomization energies are calculated using basis set TZVP (Ref. [4])

[b] The experimental atomization with zero-point-energy removed (Ref. [21])

[c] The mean absolute deviation of atomization energies of diatomic and polyatomic molecules from experiment listed in Tables 4 and 5

hartree and 1.68%, respectively, which are the best results among all the correlation energies. However, the MAD of the atomization energies for all tested molecules including the diatomic and polyatomic molecules from TPSSτ3EC is 4.93 kcal/mol, which is larger than those from TPSSτ1 (3.62 kcal/mol) and TPSSτ3 (3.52 kcal/mol). The total atomic energies from TPSSτ3EC, TPSSτ3AE, TPSSτ1 and TPSSτ3, as well as the exact total atomic energies, are listed in Table 3. The MAD and MAPD from TPSSτ3AE in Table 3 are 0.0074 hartree and 0.02%, respectively, which are the best results compared with those from TPSSτ3EC, TPSSτ1 and TPSSτ3. Unfortunately, the MAD of all tested atomization energies from TPSSτ3AE in Table 5 is 9.97 kcal/mol, which is the worst among all the methods involved. This suggests that only optimizing the parameters by fitting the correlation energies or total atomic energies alone does not give optimal results for the atomization energies. It is well-known that the conventional correlation defined within the HF-based partitioning of the many-electron energy is generally different from the KS-based partitioning [93]. The difference is small for light atoms, whereas this is not the case for heavy atoms and for molecules in general [94]. This might be one of reasons that TPSSτ3EC failed. So, we have to abandon the earlier used method [7,14], and follow the same strategy of optimizing the adjustable parameters in the τ1 meta-GGA functional [4,41] as for the Bmτ1 and Oτ2 functionals. The optimization strategy has been adopted within the hybrid schemes [10,95] and also some more recent meta-GGA functionals [5,23,28–30]. We perform a specific optimization of parameters in the τ1 correlation for a given exchange partner in a way to achieve optimal KS-DFT results for atomization energies of covalent molecules and interaction energies of weakly bound complexes, as well as for atomic correlation energies in the training set. This would lead to different optimal parameter values in the E_C functional for different exchange counterparts. Our newly reparametrized meta-GGA exchange-correlation functional is referred to as "TPSSτ3" to distinguish it from the previously named Bmτ1 [4], Oτ1, and Oτ2 [41] functionals. The parameters for τ1, τ2, τ3EC, τ3AE, and τ3 are summarized in Table 6.

These parameters are optimized by minimizing the following training function by solving the KS orbital equations

Table 6 The parameters used in the Bmτ1, Oτ1, TPSSτ1, Oτ2, TPSSτ3EC, TPSSτ3AE, and TPSSτ3

E_{XC}	α_e	$b3$	C_p	γ_2	β_2
TPSSτ3EC	1.31413	1.46596	0.09374	6.13425	−0.22241
TPSSτ3AE	1.37015	1.47000	0.04501	−6.08406	0.0
Bmτ1[a], Oτ1[b], TPSSτ1	1.299	1.470	0.045	0.175	0.0
Oτ2[b]	1.317	1.460	0.063	0.180	0.0
TPSSτ3	1.29035	1.46262	0.02851	0.17502	0.0

[a] Ref. [4]
[b] Ref. [41]

in a fully self-consistent way for the TPSS exchange and in a non-self-consistent way for the τ1 correlation.

$$F^{\text{training}} = \sum_{i=1}^{n} |E_i - E_i^{\text{ref}}| w_i \tag{38}$$

Here E_i and E_i^{ref} are the calculated energy and the reference energy in the training set, respectively. All energies are in kcal/mol except for correlation energies (in hartree). Each energy property has been associated with a certain weight. The weights w_i are adjusted to give a reasonable balance of different contributions on the basis of the work of Handy [8], Truhlar [5], and Goddard [10]. For the correlation energies of four light atoms and the interaction energies of the hydrogen-bonded and the van der Waals complexes, the weight of 100 is used. For the atomization energies of the covalent molecules, unit weight is used. All fitting calculations are performed using the A-pVTZ basis set and the GEN-A2 auxiliary basis set.

6 Results and discussion

6.1 Atomic correlation energies

Table 2 lists the calculated atomic correlation energies using a series of τ1 functionals and also two sets of best estimated exact correlation energies, E_C(I) [96] and E_C(II) [97]. E_C(I) is the most frequently used set, while E_C(II) is the revised version in light of imprecise experimental values for the ionization potentials and the Lamb shift corrections. The deviations between them increase with atomic weight. Due to the uncertainty of exact correlation energies for the heavier atoms, we compare the calculated atomic correlation energies from the selected DFT methods with the two reference sets. We can see from Table 2 that the calculated correlation energy of each atom from τ3 is slightly larger than that of the corresponding one from either τ1 or τ2. For the four key light atoms of C, N, O, and F, all the calculated correlation energies are close to those from the two reference sets. The atomic correlation energies from τ1, τ2, and τ3 are closer to E_C (II) than to E_C (I), although the heavy atoms from Ne to Ar are not included in the training set.

6.2 Atomization energies in the test set

For the atomization energies and each functional combination, we report only a statistical summary of deviations of calculated values. This includes the relative deviation (RD), the mean deviation (MD), and the mean absolute deviation (MAD) within the test set. In this section, we use the following sign convention: deviation = theory – experiment. The deviations, including the relative deviations, the mean deviations, and the mean absolute deviations for atomization energies of diatomic molecules in the test set, are listed in Table 4. The nonempirical TPSS meta-GGA does not give a good prediction for the atomization energies of the diatomic molecules as we expected. The semiempirical Bmτ1, TPSSτ1 and TPSSτ3 obtained better results for the atomization energies of the diatomic molecules in the test set than the nonempirical TPSS meta-GGA. The ability of the considered exchange-correlation schemes to reproduce the atomization energies of the diatomic molecules in decreasing order appears to be

Bmτ1 > TPSSτ1 > TPSSτ3 > TPSS

The TPSS and TPSSτ1 meta-GGAs underestimate the atomization energies for most of the diatomic molecules by 0.96 and 0.98 kcal/mol on the average, respectively. The difference of MAD of Bmτ1 and TPSSτ1 is 0.46 kcal/mol, which mainly comes from the different exchange partners used.

The deviation of atomization energies of polyatomic molecules from experiment at experimental geometries are listed in Table 5. TPSSτ1 and TPSSτ3 give better results for these polyatomic molecules in the test set than Bmτ1 and TPSS. The MAD (7.97 kcal/mol) of the atomization energies of the polyatomic molecules from TPSS is quite large. When we focus our attention on the relative deviations of atomization energies of the polyatomic molecules, the polyatomic molecules with the largest error in the calculated atomization energies are CH_4, C_2H_6, C_6H_6 (benzene), C_4H_6 (1,3-butadiene), C_4H_5N (pyrrole) and C_5H_5N (pyridine) for TPSS. In particular, the TPSS meta-GGA has difficulties to predict the atomization energies for the aromatic compounds in the test set. Meanwhile, the Bmτ1, TPSSτ1 and TPSSτ3 meta-GGAs give quite good descriptions for the aromatic compounds

Table 7 The calculated interaction energies, E_{int}, (in kcal/mol) for hydrogen-bonded and van der Waals complexes using Bmτ1, TPSSτ1, and TPSSτ3 with the same basis set A-PVTZ

Complex	E_{int} (Bmτ1)	E_{int} (TPSS)	E_{int} (TPSSτ1)	E_{int} (TPSSτ3)	E_{int} (Ref.)
$(H_2O)_2$	4.79	5.51	6.08	5.29	5.02[a]
$(NH_3)_2$	2.94	2.88	3.59	2.99	3.17[a]
$(CH_4)_2$	1.33	−0.17	1.26	0.67	0.53[a]
$(C_2H_2)_2$	1.82	−0.28	1.85	1.24	1.34[b]
MAD	0.44	0.78	0.70	0.17	
MAPD	49.65%	67.97%	52.54%	11.23%	

MAD and *MAPD* are mean absolute (percent) deviations from the best estimates

[a] The interaction energies are obtained by high level ab initio calculations at the CCSD(T)/cc-pVQZ geometries and deformation energies of monomers are not included (Ref. [77])

[b] The interaction energy are obtained by W1 theory (Ref. [75])

compared to TPSS. The MADs of the atomization energies of all the diatomic and polyatomic molecules in the test set for Bmτ1, TPSS, TPSSτ1, and TPSSτ3 are 3.62, 6.04, 3.42, and 3.52 kcal/mol, respectively. This shows that the TPSSτ1 and TPSSτ3 functionals give slightly better descriptions of the atomization energies of the molecules in the test set than Bmτ1 and TPSS. The τ1 series of exchange-correlation functionals (Bmτ1, TPSSτ1 and TPSSτ3) are able to describe the covalent molecules better than TPSS. The MAD of atomization energies of all the diatomic and polyatomic molecules in the test set for TPSSτ3 is only 0.1 kcal/mol larger than for TPSSτ1. The performance for covalent molecules including diatomic and polyatomic molecules in the test set for the four exchange-correlation functionals concerned decreases in the following order:

TPSSτ1 > TPSSτ3 > Bmτ1 > TPSS

6.3 Interaction energies

The calculated interaction energies for the hydrogen-bonded and van der Waals complexes using Bmτ1, TPSSτ1, and TPSSτ3 with the same basis set A-PVTZ and the reference interaction energies are tabulated in Table 7. TPSSτ1 gives worse results for the hydrogen-bonded complexes and the van der Waals complexes than Bmτ1 and TPSSτ3. This shows that the original TPSS meta-GGA does not match well the τ1 meta-GGA with the original values of parameters, which were obtained by matching the modified Becke88 GGA exchange. Thus, it is crucial to reoptimize the parameters in the τ1 meta-GGA correlation model when different exchange parts are used. The newly reparametrized TPSSτ3 gives the best results for the hydrogen-bonded and van der Waals complexes in the test set. The MAPD of interaction energies of the weak interactions from TPSSτ3 is 11.23%, which is much smaller than that from Bmτ1 (49.65%). There are two main reasons: (1) Different exchange counterparts are used for the two DFT methods. TPSS meta-GGA exchange is able to describe the van der Waals complexes better than Becke88 GGA exchange. We can see this from the enhancement factors of Becke88 [7] and TPSS [6] exchanges in Fig. 1. (2) Different reference geometries and interaction energies are used during the parameter optimization. The experimental geometry and the interaction energy of the water dimer [98] were used in the Bmτ1 training set while the high level ab initio CCSD(T)/cc-pVQZ geometries [77] and the theoretical interaction energies of the water dimer [77] and the ethene dimer [75] are adopted in the TPSSτ3 training set. For example, the experimental O–O distance and the interaction energy of the water dimer [98] are 2.982 Å and 5.44 ± 0.7 kcal/mol, respectively. Those obtained from high level ab initio calculations [77] are 2.916 Å and 5.02 kcal/mol.

Special attention should be paid to the two van der Waals interactions in the test set. The interaction energies of the methane dimer and the ethene dimers calculated from TPSS are −0.17 and −0.28 kcal/mol with the wrong sign. This shows that the force between the two monomers (methane or ethene) predicted by TPSS is repulsive instead of attractive. Bmτ1 and TPSSτ1 greatly overestimate the interaction energies for the two van der Waals interactions. Thus, on average, TPSSτ3 gives the best description of the covalent molecules, the hydrogen-bonded complexes and the van der Waals interactions in the test set.

7 Conclusions

The TPSS meta-GGA exchange-correlation functional and the τ1 meta-GGA correlation functional have been implemented in the deMon2k code in a fully self-consistent and in a non-self-consistent fashion, respectively. The TPSS exchange and the τ1 correlation are combined for the first time at the meta-GGA level of density functional theory. The parameters in the τ1 meta-GGA correlation are reoptimized, producing a new reparametrized TPSSτ3 meta-GGA DFT method. The results of the atomization energies for the covalent molecules and the interaction energies for the hydrogen-bonded and the van der Waals complexes in the test set obtained from TPSSτ3 are compared with those from Bmτ1, TPSSτ1 and TPSS. Bmτ1 gives the best prediction of the diatomic covalent molecules in the test set; TPSSτ1 gives the best prediction of the polyatomic covalent molecules in the test set; TPSSτ3 gives the best prediction of the hydrogen-bonded and the van der Waals complexes in the test set. On average, TPSSτ3 gives satisfactory results for the atomization energies of the covalent molecules and the interaction energies of the hydrogen-bonded complexes and van der Waals complexes in the test set compared to Bmτ1, TPSSτ1 and TPSS. The τ1 series of exchange-correlation functionals (Bmτ1, TPSSτ1 and TPSSτ3) can describe well the aromatic compounds in the test set, where the TPSS meta-GGA meets difficulties. It is encouraging that TPSSτ3 obtained satisfactory results for the covalent molecules, the hydrogen-bonded and the van der Waals complexes in the test set. This indicates that the τ1 meta-GGA correlation model could be a good platform to further develop new density functionals that can describe the weak interactions for the relevant intermolecular distance (the 2.9–3.7 Å range).

We are fully aware that the present test set is small and that further tests and probably parameter adjustments will be necessary for more complex van der Waals systems. Such tests and extensions to other classes of systems (charge-transfer complexes, transition-metal complexes, etc) will be the subject of future studies.

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