Does One-Third Scheme of PBE0 Functional Dominate Over PBE0 for Electronic Properties of Transition Metal Compounds?

M. Alipour*

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

The one-third paradigm of PBE0 density functional, PBE0-1/3, has shown to be a successful method for various properties of molecules containing main group elements. In this paper, the applicability of PBE0-1/3 is put into broader perspective for transition metals chemistry. As a comparative study, the performance of PBE0 and PBE0-1/3 has been assessed for geometries and vibrational frequencies of some transition metal hydrides and molecules containing transition metals, and static dipole polarizabilities and dipole moments for transition metal halides. The numerical data show that although PBE0-1/3 performs better than the parent PBE0 for response properties of small molecules, it does not approach the quality of PBE0 for structural parameters. Overall, the results of this investigation suggest that there is no real incentive to use PBE0-1/3 in place of PBE0 for calculations involving transition metals.

INTRODUCTION

The computational simplicity and reasonable accuracy of Kohn-Sham density functional theory (DFT) [1-3] has led to its current status as the most frequently applied method for a wide range of systems and properties. The story behind the success of DFT is the search for the exchange-correlation (XC) functional. Therefore, finding new accurate XC functionals is of paramount importance in DFT. Currently, computational chemists have a wide variety of density functionals at their disposal, ranging from local density approximation (LDA) to double-hybrid (DH) density functionals. In the present work, the class of density functionals under study is the hybrid functionals.

In 1993, Becke [4] presented the combination of the generalized gradient approximation (GGA) and the Hartree-Fock (HF) exchange in a single XC scheme. This idea was further developed to create a lineage of functionals, hybrid functionals, which are rooted in the adiabatic connection formula,

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*Corresponding author. E-mail: malipour@shirazu.ac.ir

$$E_{xc} = \int_0^1 U_{xc,\alpha}\, d\alpha \tag{1}$$

where

$$U_{xc,\alpha} = \langle \Psi_\alpha | \hat{V}_{ee} | \Psi_\alpha \rangle - \frac{1}{2} \iint \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}\, d\mathbf{r}' \tag{2}$$

and Ψ_α is the wave function that minimizes $\langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle$ under the constraint of producing the given density $n(\mathbf{r})$,

$$\Psi_\alpha = \underset{\Psi \to n(\mathbf{r})}{\text{Min}} \langle \Psi | \hat{T} + \alpha \hat{V}_{ee} | \Psi \rangle \tag{3}$$

A first-principle rationale of the HF and KS mixing has been given by Perdew, Ernzerhof, and Burke [5]. Later on, Adamo and Barone [6] and, in parallel, Ernzerhof and Scuseria [7] defined the PBE0 model as a parameter-free hybrid functional,

$$E_{xc} = E_{xc}^{\text{PBE}} + a_0 \left(E_x^{\text{HF}} - E_x^{\text{PBE}} \right) \tag{4}$$

in which $a_0 = 1/4$. This model is one of the widely used functionals and gives good performances for a wide variety of systems [8-12].

In general, $a_0 = n^{-1}$ is considered as the lowest order of the perturbation theory providing a realistic description of the systems under investigation. However, since for atomization energies of the molecules of the G1 dataset the fourth-order Møller-Plesset perturbation theory is adequate, $n = 4$ was considered in PBE0. On the other hand, Cortona [13] has shown that other values of the theoretical mixing coefficient a_0 can be chosen which actually have the same theoretical argument. On this basis, in a most recent communication, Guido *et al.* [14] proposed the recipe of one-third ($a_0 = 1/3$) as a mixing coefficient for the PBE0 functional and presented the PBE0-1/3 model. Using various benchmarks including atomization energies, weak interactions, hydrogen-bond length optimizations, dissociation energies, and vertical excitation energies they have claimed that PBE0-1/3 generally performs better than the parent PBE0. In light of these findings, we became interested in studying the performance of PBE0-1/3 for transition metal compounds. Accordingly, the main concern of the present work is a comparative investigation on the performance of PBE0 and PBE0-1/3 models for some properties of molecules containing transition metals.

The rest of this paper is organized as follows. In the following section, we expose the details of calculations. Then, a section is provided in which the results and discussion of the general trends of the benchmark calculations are covered. Finally, we conclude the paper highlighting the main inferences in the last section.

COMPUTATIONAL DETAILS

The systems and molecular properties investigated in our study included the geometries and vibrational frequencies for 3d transition metal hydrides (following previous suggestion these molecules provide a sensitive test for XC functionals [15]) and several molecules containing transition metals, static dipole polarizabilities for some of 4d and 5d transition metal halides, and dipole moments for 4d transition metal monofluorides and monochlorides for which experimental data were available [16-19]. Several basis sets were used in our calculations. Geometries and vibrational frequencies were computed using Pople's 6-311++G(3df,2pd) basis set [20,21]. In the case of dipole polarizabilities and dipole moments calculations, Dunning's aug-cc-pVTZ [22-24] and SDD [25-28] basis sets were used for main group elements and transition metals, respectively. We employed the Gaussian09 suite of codes [29] for all the runs.

RESULTS AND DISCUSSION

The numerical results for the mentioned properties are reported in Tables 1-4. Table 5 summarizes the statistical measures for the performance of PBE0 and PBE0-1/3 functionals. Figure 1 is the graphical representation of mean unsigned relative error (MUE) and root mean square relative error (RMSE) computed on different test sets. First, a glance

Table 1. Bond Lengths (r/Å) and Vibrational Frequencies (ω/cm^{-1}) for the First-row Transition Metal Hydrides (MH) Computed with PBE0 and PBE0-1/3 Models Compared with Experiment

	PBE0		PBE0-1/3		Experiment[a]	
MH	r	ω	r	ω	r	ω
ScH	1.748	1631	1.745	1638	1.775	1596
CrH	1.663	1618	1.667	1605	1.662	1615
MnH	1.727	1538	1.731	1528	1.740	1547
FeH	1.554	1752	1.561	1729	1.609	1821
CoH	1.540	1758	1.550	1727	1.513	1927
NiH	1.521	1785	1.532	1748	1.454	2001
CuH	1.485	1855	1.490	1833	1.463	1942

[a]Refs. [30-37].

Table 2. Bond Lengths (r/Å) for Some First-row Transition Metal Compounds Computed with PBE0 and PBE0-1/3 Models Compared with Experiment

Molecule (point group)	PBE0	PBE0-1/3	Experiment[a]
CrO ($C_{\infty v}$)			
r (C-O)	1.607	1.613	1.615
TiCl$_4$ (T_d)			
r (Ti-Cl)	2.162	2.157	2.170
CuCN ($C_{\infty v}$)			
r (Cu-C)	1.843	1.852	1.832
r (C-N)	1.156	1.152	1.157
FeCO ($C_{\infty v}$)			
r (Fe-C)	1.718	1.725	1.727
r (C-O)	1.163	1.160	1.159
VOF$_3$ (C_{3v})			
r (V-O)	1.541	1.531	1.569
r (V-F)	1.715	1.710	1.729
Ni(CO)$_4$ (T_d)			
r (Ni-C)	1.822	1.822	1.838
r (C-O)	1.132	1.128	1.141

[a]Refs. [38-43].

Table 3. Computed Values of the Static Dipole Polarizabilities (au) for Second- and Third-row Transition Metal Halides Computed with PBE0 and PBE0-1/3 Models Compared with CCSD(T) Results

Molecule	PBE0	PBE0-1/3	CCSD(T)
YF	127.55	128.08	126.27
NbF	73.99	74.91	85.03
MoF	55.71	55.77	64.67
TcF	54.64	54.30	54.97
RuF	50.52	50.12	43.60
RhF	27.99	26.56	26.18
PdF	27.21	25.73	24.69
AgF	24.07	22.69	22.54
CdF	39.56	39.34	41.68
YCl	140.05	140.26	137.56
NbCl	83.39	83.63	95.77
MoCl	67.57	66.56	75.39
TcCl	70.14	69.51	70.11
RuCl	69.41	62.06	52.32
RhCl	50.98	49.32	48.71
PdCl	45.02	43.53	42.67
AgCl	41.82	40.45	40.68
CdCl	55.97	55.63	57.76
AuF	28.93	28.04	30.68
HfF	91.35	91.79	82.58
HgF	35.25	35.15	35.82
OsF	44.62	36.95	41.09
ReF	46.77	46.20	47.04
WF	52.85	52.84	59.32

Table 4. Computed Values of the Dipole Moments (D) for Some Second-row Transition Metal Halides Computed with PBE0 and PBE0-1/3 Models Compared with Experiment

Molecule	PBE0	PBE0-1/3	Experiment[a]
YF	1.975	1.981	1.828
AgF	5.984	6.182	6.22
YCl	2.593	2.638	2.587
AgCl	5.798	6.021	6.22

[a]Refs. [16-19].

Table 5. Comparison of the Performance of PBE0 and PBE0-1/3 Functionals for the Studied Properties in This Investigation. The Statistical Descriptors are Mean Unsigned Relative Error (MUE) and Root Mean Square Relative Error (RMSE).

Test sets	PBE0		PBE0-1/3	
	MUE	RMSE	MUE	RMSE
BLTMH[a]	0.020	0.024	0.021	0.027
BLTM[b]	0.007	0.008	0.008	0.010
VFTMH[c]	0.044	0.058	0.055	0.069
DP4d-5dTMX[d]	0.077	0.104	0.064	0.084
DM4dTMX[e]	0.047	0.056	0.035	0.046

[a]Bond length of 3d transition metal hydrides. [b]Bond length of transition metal molecules. [c]Vibrational frequency of 3d transition metal hydrides. [d]Dipole polarizability of 4d and 5d transition metal halides. [e]Dipole moment of 4d transition metal halides.

to our statistical analysis (Table 5 and Fig. 1) is sufficient to conclude that the two functionals PBE0 and PBE0-1/3 have almost the same accuracy in all cases. However, let us compare the performance of these functionals in details.

The results of Tables 1 and 2 show that both PBE0 and PBE0-1/3 yield bond lengths which are in agreement with the experimental values. Moreover, observe, from Table 1, that there are no clear geometrical trends in metal hydrides. As shown in Figs. 1a and 1b, for geometries of metal hydrides and molecules containing transition metals, the MUEs of PBE0 and PBE0-1/3 are very close and their differences are not significant. These results reveal that increasing the HF exchange from 25% in PBE0 to 33.33%

in PBE0-1/3 does not affect the geometries in this case. Usually, including a larger percentage of HF exchange deteriorates the structures, if this effect is not compensated by correlation [14,44]. Interestingly, both functionals outperform parameter-free double-hybrid PBE0-DH model (MUE = 0.038 and RMSE = 0.05) for geometries of metal hydrides. Note that the PBE0-DH includes 50% HF exchange and 12.5% MP2 contribution to the correlation energy. Since hybrid density functional calculations are much less expensive than double-hybrid ones, it is encouraging that some of the hybrid functionals perform better than their DH counterparts. In the case of vibrational frequencies of metal hydrides, Fig. 1c, the MUE of PBE0
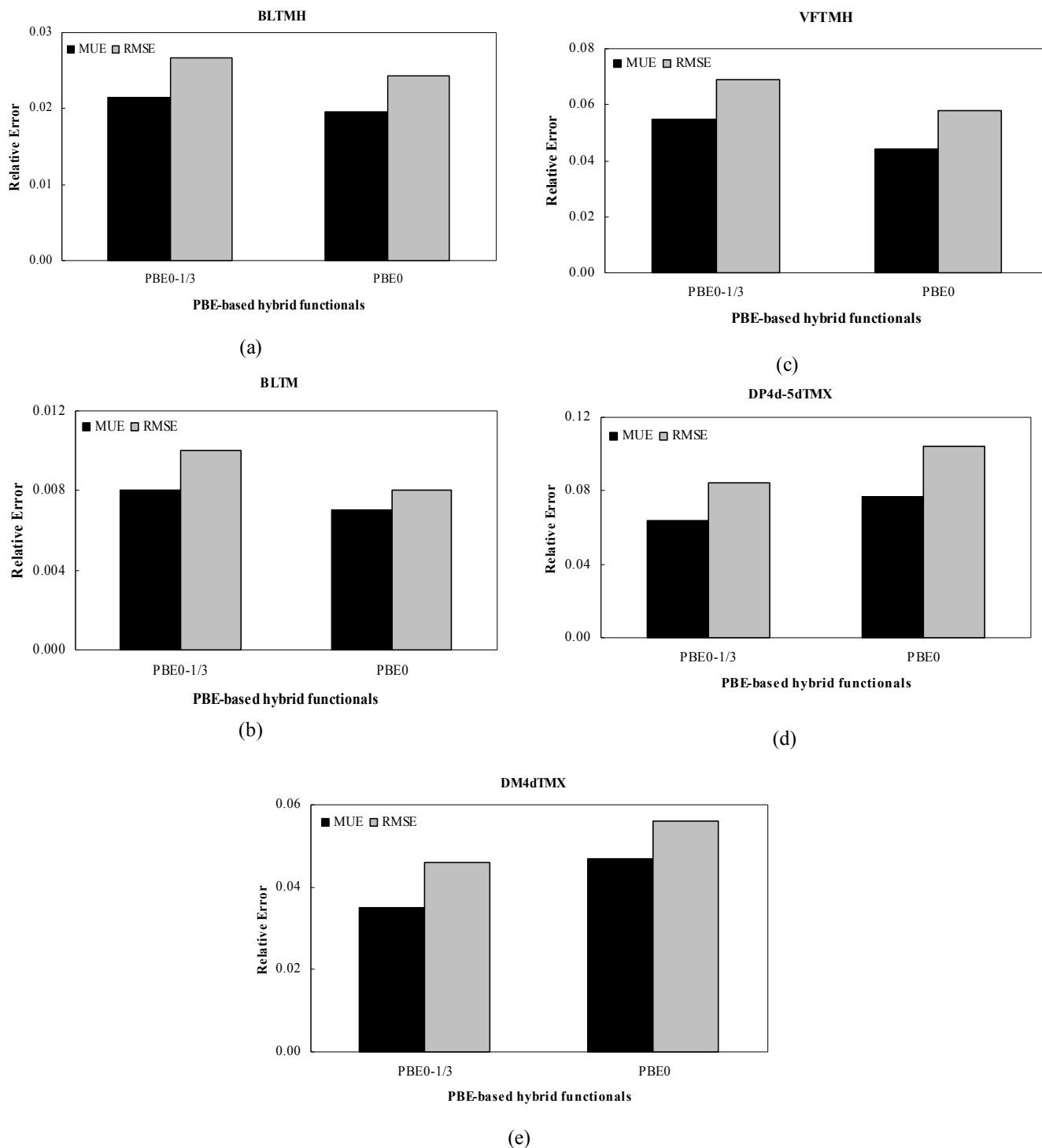
Fig. 1. Pictorial representation of mean unsigned relative error (MUE) and root mean square relative error (RMSE) for various test sets. (a) Bond length of 3d transition metal hydrides (BLTMH), (b) Bond length of transition metal molecules (BLTM), (c) Vibrational frequency of 3d transition metal hydrides (VFTMH), (d) Dipole polarizability of 4d and 5d transition metal halides (DP4d-5dTMX), and (e) Dipole moment of 4d transition metal halides (DM4dTMX).

(0.044) is smaller than those of PBE0-1/3 (0.055). However, the PBE0-1/3 MUE is close to those obtained from PBE0-DH (0.052).

Next, the performance of PBE0-1/3 is evaluated for response properties of several transition metal systems. The calculation of how a small perturbation can affect the ground state energy allows one to calculate some important properties from linear response theory with the use of DFT and compare the applicability of functionals in this respect. Considering the corresponding results for static dipole polarizabilities and dipole moments of 4d and 5d transition metal halides, Tables 3 and 4, we first see that both PBE0 and PBE0-1/3 overestimate the polarizabilities and dipole moments for some molecules whereas the same properties are underestimated by the two methods for some other systems. Moreover, Figs. 1d and 1e reveal that more accurate results are obtained for polarizabilities and dipole moments in passing from PBE0 to PBE0-1/3, highlighting the importance of HF exchange in the calculations of electric response properties. Generally, the obtained MUEs show that the PBE0-1/3 error for dipole polarizabilities and dipole moments, respectively, is about 17% and 25% lower than that of PBE0.

We have also examined the performance of PBE0 and PBE0-1/3 functionals for dipole polarizabilities of two large compounds containing transition metals, eclipsed conformer of ferrocene ($Fe(C_5H_5)_2$) and a molecule from the group IV tetrachlorides ($TiCl_4$), for which experimental dipole polarizabilities are available as 126.2 au [45] and 101.4 au [46], respectively. For polarizabilities of $Fe(C_5H_5)_2$ and $TiCl_4$ at their experimental geometries [47-49], respectively, we obtained the unsigned errors 0.03 and 0.08 from PBE0 and 0.05 and 0.09 from PBE0-1/3. However, these results show that for dipole polarizabilities of more complex systems the errors of the two functionals are close to each other.

CONCLUDING REMARKS

In summary, we explored the behavior of a recently proposed version of PBE0 functional, PBE0-1/3, in predicting various properties such as bond lengths, vibrational frequencies, static dipole polarizabilities, and dipole moments of molecules containing transition metals.

We found that although PBE0-1/3 works better than PBE0 for dipole polarizabilities and dipole moments of small molecules, it provides results for geometries and vibrational frequencies of about the same quality as PBE0. On the whole, our results suggest that there is no real incentive to use PBE0-1/3 in place of PBE0 for calculations involving transition metals, at least for properties studied here. Lastly, it remains challenging to develop a generally density functional resolving all the qualitative failures of previous approximations at a reasonable computational cost.

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