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# Can Kohn–Sham density functional theory predict accurate charge distributions for both single-reference and multi-reference molecules?†

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Dipole moments are the first moment of electron density and are fundamental quantities that are often available from experiments. An exchange–correlation functional that leads to an accurate representation of the charge distribution of a molecule should accurately predict the dipole moments of the molecule. It is well known that Kohn–Sham density functional theory (DFT) is more accurate for the energetics of single-reference systems than for the energetics of multi-reference ones, but there has been less study of charge distributions. In this work, we benchmark 48 density functionals chosen with various combinations of ingredients, against accurate experimental data for dipole moments of 78 molecules, in particular 55 single-reference molecules and 23 multi-reference ones. We chose both organic and inorganic molecules, and within the category of inorganic molecules there are both main-group and transition-metal-containing molecules, with some of them being multi-reference. As one would expect, the multi-reference molecules are not as well described by single-reference DFT, and the functionals tested in this work do show larger mean unsigned errors (MUEs) for the 23 multi-reference molecules than the single-reference ones. Five of the 78 molecules have relatively large experimental error bars and were therefore not included in calculating the overall MUEs. For the 73 molecules not excluded, we find that three of the hybrid functionals, B97-1, PBE0, and TPSSh (each with less than or equal to 25% Hartree–Fock (HF) exchange), the range-separated hybrid functional, HSE06 (with HF exchange decreasing from 25% to 0 as interelectronic distance increases), and the hybrid functional, PW6B95 (with 28% HF exchange) are the best performing functionals with each yielding an MUE of 0.18 D. Perhaps the most significant finding of this study is that there exists great similarity among the success rate of various functionals in predicting dipole moments. In particular, of 39 functionals designed as general-purpose functionals and that do not have a global value of 100% HF exchange, the average MUE is 0.23 D, with a standard deviation of only 0.04 D. Among gradient approximations, which are especially interesting because of their speed and portability, the best overall performance is by PBE, HCTH/407, OLYP, OreLYP, and GAM, each with MUE of 0.22 D.

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## 1. Introduction

Kohn–Sham density functional theory (KS-DFT) has been very successful for calculating energetic quantities like reaction energies and barrier heights and for calculating geometries of molecules and lattice constants of solids.[1–5] A question that has been less well studied is, how accurate are the electron densities that it predicts? The first nonzero moment of the charge density of a neutral molecule is its dipole moment,[6–8] and so – before one considers more detailed characteristics of charge distributions – it is important to first examine how well KS-DFT can predict that leading moment. The accuracy of KS-DFT depends on the quality of the approximate density functional employed (the exact functional is not known), and currently available functionals are more accurate for single-reference (SR) systems (systems whose electronic structure can be well described by a single configuration state function) than for multi-reference (MR) systems (systems with near-degeneracy correlation effects). In this article we examine the question of the prediction of the leading moment of the charge distribution by testing the predictions of a number of exchange–correlation functionals for a diverse set of molecules – both single-reference and multi-reference, for which experimental dipole moments are available. A particularly noteworthy feature of the present study is that the test of theory is not limited to organic chemistry or light atoms, but rather it includes a diverse set of molecular types, including compounds containing both main-group metals and transition metals.

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## 2. Computational details

A key quantity characterizing an exchange–correlation functional is the percentage of nonlocal Hartree–Fock exchange included in the functional; we call this percentage *X*. The 48 exchange–correlation functionals considered in this work are listed in Table 1, which also gives the year of publication of the functional and the value or range of *X*.

Table 1 Density functionals tested in this work

| Type | Functional | Year | $X^a$ | Ref. |
|---|---|---|---|---|
| GGA | BLYP | 1988 | 0 | 19 and 20 |
| | PBE | 1996 | 0 | 21 |
| | HCTH/407 | 2001 | 0 | 22 |
| | OLYP | 2001 | 0 | 19 and 23 |
| | PBEsol | 2008 | 0 | 24 |
| | OreLYP | 2009 | 0 | 23 and 25 |
| | SOGGA11 | 2011 | 0 | 26 |
| | HLE16 | 2017 | 0 | 27 |
| NGA | N12 | 2012 | 0 | 28 |
| | GAM | 2015 | 0 | 29 |
| meta-GGA | τ-HCTH | 2002 | 0 | 30 |
| | TPSS | 2003 | 0 | 31 |
| | M06-L | 2006 | 0 | 32 |
| | M11-L | 2011 | 0 | 33 |
| | MGGA_MS2 | 2013 | 0 | 34 |
| | HLE17 | 2017 | 0 | 35 |
| meta-NGA | MN12-L | 2012 | 0 | 36 |
| | MN15-L | 2016 | 0 | 37 |
| Hybrid GGA | BHandHLYP | 1993 | 50 | 38 |
| | B3LYP | 1994 | 20 | 19, 20, 39 and 40 |
| | B1LYP | 1997 | 25 | 41 |
| | mPW1PW | 1997 | 25 | 42 |
| | B97-1 | 1998 | 21 | 43 |
| | PBE0 | 1999 | 25 | 44 |
| | MPW1K | 2000 | 42.8 | 45 |
| | B3LYP* | 2001 | 15 | 46 |
| | CAM-B3LYP | 2004 | 19–65 | 47 |
| | MPW3LYP | 2004 | 21.8 | 48 |
| | B97-3 | 2005 | 26.93 | 49 |
| | LC-ωPBE | 2006 | 0–100 | 50 |
| | HSE06 | 2009 | 25–0 | 51 and 52 |
| | SOGGA11-X | 2011 | 40.15 | 53 |
| Hybrid GGA + MM | B3LYP-D3(BJ) | 2011 | 20 | 54 and 55 |
| Hybrid NGA | N12-SX | 2012 | 25–0 | 56 |
| Hybrid meta-GGA | τ-HCTHhyb | 2002 | 15 | 57 |
| | TPSSh | 2003 | 10 | 58 |
| | MPWB1K | 2004 | 44 | 59 |
| | M05 | 2005 | 28 | 60 |
| | M05-2X | 2005 | 56 | 61 |
| | PW6B95 | 2005 | 28 | 62 |
| | M06-HF | 2006 | 100 | 63 |
| | M06 | 2008 | 27 | 64 |
| | M06-2X | 2008 | 54 | 64 |
| | M08-HX | 2008 | 52.23 | 65 |
| | M08-SO | 2008 | 56.79 | 65 |
| | M11 | 2011 | 42.8–100 | 66 |
| Hybrid meta-NGA | MN12-SX | 2012 | 25–0 | 56 |
| | MN15 | 2016 | 44 | 5 |

[a] *X* is the percentage of HF exchange. When a range is given for *X*, the first value indicates the percentage of HF exchange for short interelectronic separations and the second value indicates the percentage of HF exchange for long interelectronic separations.

Table 2 Experimental dipole moments[a] (in debye) of 78 molecules investigated in this work

| Molecule | 2*S* + 1 | Dipole moment | Molecule | 2*S* + 1 | Dipole moment |
|---|---|---|---|---|---|
| Acetyl chloride | 1 | 2.72 | LaO | 2 | 3.21 |
| AgBr | 1 | 5.62 | LiOH | 1 | 4.50 |
| AgCl | 1 | 6.08 | Methylamine | 1 | 1.31 |
| AgI | 1 | 4.55 | Methylphosphine | 1 | 1.1 |
| AlF | 1 | 1.53 | Methylsilane | 1 | 0.73 |
| $AsH_3$ | 1 | 0.22 | MgO | 1 | 6.2 |
| Aziridine | 1 | 1.89 | $N_2O$ | 1 | 0.16 |
| Benzonitrile | 1 | 4.18 | NaCl | 1 | 9.00 |
| $BF_3NH_3$ | 1 | 5.90 | $NH_3$ | 1 | 1.47 |
| $BH_2Cl$ | 1 | 0.75 | NiH | 2 | 2.40 |
| Bromoform | 1 | 0.99 | Nitrobenzene | 1 | 4.22 |
| Bromomethane | 1 | 1.82 | Nitromethane | 1 | 3.46 |
| $CH_3I$ | 1 | 1.64 | Nitrosyl hydride | 1 | 1.62 |
| CrN | 4 | 2.31 | PbO | 1 | 4.64 |
| CrO | 5 | 3.88 | PbS | 1 | 3.59 |
| CuF | 1 | 5.77 | $PH_3$ | 1 | 0.57 |
| CuO | 2 | 4.45, 4.5 | Phenol | 1 | 1.22 |
| Dimethyl sulfoxide | 1 | 3.96 | *cis*-Propyleneimine | 1 | 1.77 |
| Ethanol | 1 | 1.44 | *trans*-Propyleneimine | 1 | 1.57 |
| FeO | 5 | 4.70 | Propyne | 1 | 0.78 |
| Fluoroacetylene | 1 | 0.72 | RbCl | 1 | 10.51 |
| Fluorosilane | 1 | 1.27 | RbF | 1 | 8.55 |
| s-*cis*-Formic acid | 1 | 1.43 | ScF | 1 | 1.72 |
| s-*trans*-Formic acid | 1 | 3.79 | ScO | 2 | 4.55 |
| GeO | 1 | 3.28 | $SeO_2$ | 1 | 2.62 |
| $H_2CO$ | 1 | 2.33 | $SO_2$ | 1 | 1.63 |
| $H_2O$ | 1 | 1.85 | SrO | 1 | 8.9 |
| $H_2S$ | 1 | 0.98 | TiH | 4 | 2.46 |
| HBr | 1 | 0.83 | TiN | 2 | 3.56 |
| HCCI | 1 | 0.03 | TiO | 3 | 2.96 |
| HCl | 1 | 1.11 | TlBr | 1 | 4.49 |
| HCN | 1 | 2.99 | TlCl | 1 | 4.54 |
| HF | 1 | 1.83 | TlF | 1 | 4.23 |
| $HfO_2$ | 1 | 7.92 | TlI | 1 | 4.61 |
| HfO | 1 | 3.43 | VN | 3 | 3.07 |
| HI | 1 | 0.45 | VO | 4 | 3.36 |
| Imidazole | 1 | 3.8 | YO | 2 | 4.52 |
| Ketene | 1 | 1.42 | $ZrO_2$ | 1 | 7.80 |
| KF | 1 | 8.59 | ZrO | 1 | 2.55 |

[a] The experimental values are from ref. 9 and 10 and references therein.

We gathered the experimental gas-phase dipole moments of 78 molecules from several sources, and the values gathered are given in Table 2. First we considered Table 10 of ref. 9, and we selected all the transition-metal containing molecules (except one) that have an experimental dipole moment (the one not included is YbF because the def2-QZVP basis set is not available for Yb). Then we considered Table VIII of ref. 10 and selected all the transition-metal containing molecules that have an experimental dipole moment. Finally we took additional molecules either from the ESI of ref. 9 or from the *CRC Handbook of Chemistry and Physics*.[11]

All calculations were carried out with the *Gaussian 09* program[12,13] or an in-house modified version[14] of *Gaussian 09*. We used the def2-TZVP[15] or the def2-QZVP[15] basis set. Note that these are all-electron basis sets for atoms in periods 1–4 (H through Kr), and they involve relativistic effective core potentials starting with period 5 (Rb and higher). All calculations reported here treat the valence electrons nonrelativistically.

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A comparison of def2-TZVP and def2-QZVP basis sets for selected functionals on selected molecules is provided in Table S1 of the ESI,† but all numbers reported in the main text are using the def2-QZVP basis set.

The quantum mechanical dipole moments reported in this paper are for consistently optimized geometries, that is, in every case the molecule's geometry is optimized with the same exchange–correlation functional and basis set as is used for calculating the dipole moment. An UltraFine grid that has 99 radial nodes and 590 angular points per node was used. In all cases we converged the self-consistent-field calculations to a stable solution and for open-shell systems where energy could be lowered even more by further breaking of symmetry, we used the "stable = opt" facility in *Gaussian 09* to converge to the most stable solution.

Two spin states were optimized using M06-L/def2-QZVP for open-shell molecules and molecules that are singlets with potentially low-energy higher spin states. The energy gaps, $\langle S^2 \rangle$ values (where $S$ is total electron spin), and dipole moments are reported in Table S2 of the ESI.† Table S2 (ESI†) shows that dipole moments can vary significantly with spin state, but in the main text we report dipole moments only for the experimental ground spin states. The experimental ground spin state for most of the molecules used here is singlet and for open-shell molecules, the experimental ground spin states reported in ref. 9 or 10 are used; the ground-state multiplicities for all the molecules are listed in Table 2.

The extent of multi-reference character was determined for all the molecules using the $B_1$ diagnostic.[16] The $B_1$ diagnostic is defined by

$$B_1 = (\mathrm{BE}_{\mathrm{BLYP}} - \mathrm{BE}_{\mathrm{B1LYP//BLYP}})/n \qquad (1)$$

where BE is equilibrium bond energy, defined by eqn (5) of ref. 16. Note that an actual BE involves spin-orbit coupling (SOC), but for the purpose of computing the $B_1$ diagnostic it is not required because it cancels in eqn (1). Because the $B_1$ diagnostic uses bond energies, one needs to compute the energies of the separated atoms using BLYP and B1LYP. For calculating the energies of the separated atoms, the spin states of atoms considered in our calculations are the experimental ground spin states as given in ref. 17

The first term of eqn (1) indicates that the bond energies were calculated using BLYP for geometries optimized using BLYP itself, and the second term indicates that the B1LYP bond energies were calculated by single-point calculations at the BLYP optimized geometries. The quantity $n$ represents the number of bonds being broken in a molecule, where a multiple bond (double, triple, *etc.*) between two atoms is treated as one bond. A system is classified single-reference if it has a $B_1$ diagnostic value less than 10 kcal mol$^{-1}$; otherwise it is classified as multi-reference. Table 3 shows that 23 of the 78 molecules were found to be multi-reference based on this criterion. The $B_1$ diagnostic is based on BLYP and B1LYP because these two functionals differ only in the percentage of HF exchange that replaces a portion of the local exchange, and all their other ingredients are the same. Inclusion of HF exchange brings in static correlation error for multireference systems, and we have found that a high $B_1$ diagnostic is usually associated with high multireference character. The criterion of 10 kcal mol$^{-1}$ was chosen based on the tests that were performed as part of ref. 16. Our suggestion that a quantity like the $B_1$ diagnostic can be used to detect multireference character was later confirmed by Fogueri *et al.*[18]

The mean unsigned errors (MUEs), which are the absolute deviations from the best estimates, for dipole moments were calculated separately for SR and MR systems along with the overall MUE.

Table 3 The $B_1$ diagnostic values (kcal mol$^{-1}$) of all molecules using def2-QZVP basis set

| Molecule | $B_1$ diagnostic | Molecule | $B_1$ diagnostic |
|---|---|---|---|
| Acetyl chloride | 2.9 | LaO | 13.5 |
| AgBr | 0.8 | LiOH | 4.3 |
| AgCl | 1.2 | Methylamine | 1.3 |
| AgI | 0.8 | Methylphosphine | 0.5 |
| AlF | 5.7 | Methylsilane | −0.2 |
| $AsH_3$ | 0.9 | MgO | 19.0 |
| Aziridine | 1.5 | $N_2O$ | 16.8 |
| Benzonitrile | 2.5 | NaCl | 0.5 |
| $BF_3NH_3$ | 2.4 | $NH_3$ | 2.0 |
| $BH_2Cl$ | 0.2 | NiH | 4.2 |
| Bromoform | 2.6 | Nitrobenzene | 3.6 |
| Bromomethane | 0.9 | Nitromethane | 5.7 |
| $CH_3I$ | 0.9 | Nitrosyl hydride | 9.6 |
| CrN | 36.4 | PbO | 20.8 |
| CrO | 27.6 | PbS | 9.1 |
| CuF | 8.4 | $PH_3$ | 0.4 |
| CuO | 15.2 | Phenol | 2.0 |
| Dimethyl sulfoxide | 1.8 | *cis*-Propyleneimine | 1.2 |
| Ethanol | 1.2 | *trans*-Propyleneimine | −7.9 |
| FeO | 30.4 | Propyne | 1.7 |
| Fluoroacetylene | 5.1 | RbCl | 0.1 |
| Fluorosilane | 0.4 | RbF | 6.7 |
| s-*cis*-Formic acid | 5.0 | ScF | 13.2 |
| s-*trans*-Formic acid | 5.1 | ScO | 22.1 |
| GeO | 16.2 | $SeO_2$ | 16.7 |
| $H_2CO$ | 4.0 | $SO_2$ | 13.2 |
| $H_2O$ | 3.3 | SrO | 17.9 |
| $H_2S$ | 0.9 | TiH | 6.3 |
| HBr | 1.3 | TiN | 34.1 |
| HCCI | 3.9 | TiO | 27.4 |
| HCl | 1.3 | TlBr | 2.3 |
| HCN | 6.8 | TlCl | 2.7 |
| HF | 4.9 | TlF | 9.1 |
| $HfO_2$ | 15.5 | TlI | 2.0 |
| HfO | 16.6 | VN | 36.8 |
| HI | 1.4 | VO | 30.7 |
| Imidazole | 2.8 | YO | 15.1 |
| Ketene | 4.4 | $ZrO_2$ | 16.9 |
| KF | 6.9 | ZrO | 20.1 |

## 3. $B_1$ diagnostics

Table 3 shows the $B_1$ diagnostic values for all 78 molecules. Of these 78 molecules, 23 have values greater than 10 kcal mol$^{-1}$ and are therefore classified as multi-reference molecules. It is interesting to note that all the organic molecules in the table are single-reference cases, and among the inorganic molecules almost all the transition-metal containing ones are multi-reference with the

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exception of transition-metal hydrides (TiH and NiH) and CuF. The inorganic main-group containing molecules that are multi-reference are GeO, MgO, $N_2O$, PbO, $SO_2$, $SeO_2$ and SrO. In comparison with the published work using $B_1$ diagnostics in ref. 16, we see that the molecules FeO, MgO, and VO, are common to both the studies, and the small differences in the diagnostic values can be attributed to the different basis sets used in the two studies.

## 4. Comparison of density functionals

Before beginning the discussion of performance of density functionals, we note that all dipole moments in this paper are computed at geometries optimized by the functional used to compute the dipole moment. (Such geometries are sometimes called consistently optimized geometries.) Thus, if a functional is to predict accurate dipole moments without cancellation of errors, it should first predict an accurate geometry and then predict an accurate charge distribution for that geometry.

First we checked the effect of basis set by comparing results obtained with the def2-TZVP and def2-QZVP basis sets for 21 molecules using 13 density functionals (see Table S1 (ESI†) for full results of this test). The MUEs obtained with the two basis sets are quite close to each other for each of the 13 functionals; the maximum difference between the MUEs with the two basis sets is 0.07 D. Additionally, with all the functionals, the def2-QZVP basis set gives a lower MUE than the def2-TZVP basis set, and therefore all the results presented in the article are for the def2-QZVP basis set.

The experimental dipole moments of five of the 78 molecules (CuF, CuO, MgO, PbO and PbS) have relatively large error bars, and the calculated values for these molecules are relegated to Table S3 of the ESI.† The dipole moments of the remaining 73 molecules calculated by GGAs and NGAs are shown in Table 4, those calculated by meta-GGAs and

Table 4 Dipole moments (in debyes) of 73 molecules as calculated using GGAs and NGAs

| Molecule | BLYP | PBE | HCTH/407 | OLYP | PBEsol | OreLYP | SOGGA11 | HLE16 | N12 | GAM | Expt. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetyl chloride | 2.86 | 2.79 | 2.76 | 2.77 | 2.78 | 2.77 | 2.58 | 2.69 | 2.83 | 2.70 | 2.72 |
| AgBr | 4.55 | 4.65 | 4.92 | 4.92 | 4.52 | 4.87 | 5.26 | 5.67 | 4.55 | 4.90 | 5.62 |
| AgCl | 4.84 | 4.91 | 5.20 | 5.16 | 4.76 | 5.11 | 5.44 | 5.89 | 4.90 | 5.31 | 6.08 |
| AgI | 3.97 | 4.13 | 4.39 | 4.41 | 4.02 | 4.36 | 4.94 | 5.17 | 3.96 | 4.29 | 4.55 |
| AlF | 1.62 | 1.50 | 1.45 | 1.45 | 1.43 | 1.45 | 1.47 | 1.21 | 1.39 | 1.49 | 1.53 |
| $AsH_3$ | 0.16 | 0.27 | 0.26 | 0.25 | 0.34 | 0.26 | 0.18 | 0.39 | 0.27 | 0.23 | 0.22 |
| Aziridine | 1.67 | 1.63 | 1.60 | 1.60 | 1.62 | 1.60 | 1.63 | 1.56 | 1.63 | 1.56 | 1.89 |
| Benzonitrile | 4.65 | 4.63 | 4.64 | 4.63 | 4.65 | 4.63 | 4.49 | 4.67 | 4.69 | 4.61 | 4.18 |
| $BF_3NH_3$ | 6.00 | 6.03 | 5.97 | 5.99 | 6.05 | 6.00 | 6.10 | 5.97 | 6.06 | 5.91 | 5.90 |
| $BH_2Cl$ | 0.52 | 0.44 | 0.50 | 0.49 | 0.40 | 0.48 | 0.35 | 0.48 | 0.56 | 0.49 | 0.75 |
| Bromoform | 0.85 | 0.85 | 0.84 | 0.84 | 0.86 | 0.84 | 0.86 | 0.78 | 0.84 | 0.83 | 0.99 |
| Bromomethane | 1.90 | 1.85 | 1.84 | 1.84 | 1.84 | 1.84 | 1.65 | 1.71 | 1.84 | 1.81 | 1.82 |
| $CH_3I$ | 1.66 | 1.65 | 1.64 | 1.63 | 1.66 | 1.63 | 1.44 | 1.48 | 1.59 | 1.62 | 1.64 |
| CrN | 3.04 | 2.95 | 2.95 | 2.98 | 2.88 | 3.05 | 2.76 | 3.08 | 2.84 | 2.65 | 2.31 |
| CrO | 3.66 | 3.54 | 3.93 | 3.74 | 3.45 | 3.83 | 3.43 | 4.56 | 3.69 | 3.66 | 3.88 |
| Dimethyl sulfoxide | 3.81 | 3.78 | 3.75 | 3.71 | 3.80 | 3.71 | 3.37 | 3.84 | 3.85 | 3.79 | 3.96 |
| Ethanol | 1.56 | 1.51 | 1.51 | 1.50 | 1.50 | 1.49 | 1.54 | 1.49 | 1.53 | 1.50 | 1.44 |
| FeO | 4.35 | 4.27 | 4.19 | 4.56 | 4.19 | 4.59 | 4.52 | 5.42 | 4.42 | 4.01 | 4.70 |
| Fluoroacetylene | 0.56 | 0.48 | 0.47 | 0.47 | 0.44 | 0.47 | 0.32 | 0.48 | 0.58 | 0.45 | 0.72 |
| Fluorosilane | 1.31 | 1.26 | 1.25 | 1.25 | 1.23 | 1.24 | 1.07 | 1.19 | 1.30 | 1.29 | 1.27 |
| s-*cis*-Formic acid | 1.47 | 1.49 | 1.51 | 1.49 | 1.52 | 1.49 | 1.49 | 1.66 | 1.56 | 1.52 | 1.43 |
| s-*trans*-Formic acid | 3.77 | 3.76 | 3.76 | 3.73 | 3.80 | 3.73 | 3.74 | 3.90 | 3.87 | 3.73 | 3.79 |
| GeO | 3.27 | 3.16 | 3.20 | 3.17 | 3.10 | 3.16 | 3.22 | 3.37 | 3.26 | 3.26 | 3.28 |
| $H_2CO$ | 2.25 | 2.21 | 2.20 | 2.18 | 2.20 | 2.18 | 2.03 | 2.29 | 2.29 | 2.19 | 2.33 |
| $H_2O$ | 1.87 | 1.87 | 1.87 | 1.86 | 1.89 | 1.86 | 1.93 | 1.88 | 1.90 | 1.84 | 1.85 |
| $H_2S$ | 0.98 | 1.02 | 1.04 | 1.02 | 1.05 | 1.02 | 1.09 | 1.05 | 1.07 | 1.07 | 0.98 |
| HBr | 0.85 | 0.89 | 0.88 | 0.87 | 0.92 | 0.88 | 0.97 | 0.87 | 0.87 | 0.85 | 0.83 |
| HCCI | 0.26 | 0.22 | 0.22 | 0.24 | 0.20 | 0.23 | 0.32 | 0.23 | 0.30 | 0.22 | 0.03 |
| HCl | 1.11 | 1.13 | 1.14 | 1.12 | 1.15 | 1.13 | 1.19 | 1.11 | 1.16 | 1.14 | 1.11 |
| HCN | 2.96 | 2.95 | 2.95 | 2.92 | 2.97 | 2.93 | 3.07 | 2.96 | 2.97 | 2.94 | 2.99 |
| HF | 1.81 | 1.80 | 1.80 | 1.79 | 1.82 | 1.79 | 1.82 | 1.80 | 1.85 | 1.78 | 1.83 |
| $HfO_2$ | 7.45 | 7.44 | 7.47 | 7.45 | 7.41 | 7.43 | 7.71 | 7.56 | 7.54 | 7.42 | 7.92 |
| HfO | 3.38 | 3.24 | 3.45 | 3.45 | 3.17 | 3.33 | 2.70 | 4.03 | 3.23 | 3.21 | 3.43 |
| HI | 0.39 | 0.43 | 0.42 | 0.42 | 0.48 | 0.43 | 0.49 | 0.41 | 0.38 | 0.37 | 0.45 |
| Imidazole | 3.66 | 3.67 | 3.66 | 3.63 | 3.71 | 3.63 | 3.71 | 3.63 | 3.65 | 3.66 | 3.8 |
| Ketene | 1.47 | 1.45 | 1.44 | 1.43 | 1.46 | 1.43 | 1.33 | 1.57 | 1.54 | 1.38 | 1.42 |
| KF | 8.24 | 8.14 | 8.27 | 8.18 | 8.00 | 8.16 | 8.35 | 7.98 | 8.06 | 8.38 | 8.59 |
| LaO | 4.25 | 3.88 | 3.59 | 3.65 | 3.82 | 3.71 | 3.61 | 4.81 | 3.70 | 3.77 | 3.21 |
| LiOH | 4.25 | 4.27 | 4.31 | 4.26 | 4.24 | 4.25 | 3.66 | 4.35 | 4.19 | 4.40 | 4.50 |
| Methylamine | 1.28 | 1.27 | 1.26 | 1.27 | 1.26 | 1.27 | 1.25 | 1.16 | 1.21 | 1.25 | 1.31 |
| Methylphosphine | 1.10 | 1.18 | 1.21 | 1.17 | 1.23 | 1.18 | 1.09 | 1.28 | 1.23 | 1.29 | 1.1 |
| Methylsilane | 0.78 | 0.84 | 0.84 | 0.82 | 0.88 | 0.83 | 0.82 | 0.84 | 0.82 | 0.88 | 0.73 |
| $N_2O$ | 0.07 | 0.14 | 0.16 | 0.14 | 0.18 | 0.14 | 0.20 | 0.18 | 0.05 | 0.20 | 0.16 |
| NaCl | 8.46 | 8.52 | 8.57 | 8.43 | 8.51 | 8.41 | 6.80 | 8.83 | 8.42 | 8.79 | 9.00 |
| $NH_3$ | 1.52 | 1.54 | 1.53 | 1.53 | 1.55 | 1.53 | 1.59 | 1.48 | 1.49 | 1.51 | 1.47 |

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Table 4 (*continued*)

| Molecule | BLYP | PBE | HCTH/407 | OLYP | PBEsol | OreLYP | SOGGA11 | HLE16 | N12 | GAM | Expt. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| NiH | 2.06 | 2.15 | 2.27 | 2.29 | 2.11 | 2.27 | 2.60 | 2.70 | 2.30 | 2.20 | 2.40 |
| Nitrobenzene | 4.66 | 4.51 | 4.46 | 4.48 | 4.46 | 4.47 | 4.29 | 4.49 | 4.68 | 4.38 | 4.22 |
| Nitromethane | 3.48 | 3.41 | 3.36 | 3.36 | 3.41 | 3.36 | 3.13 | 3.34 | 3.50 | 3.32 | 3.46 |
| Nitrosyl hydride | 1.62 | 1.60 | 1.54 | 1.54 | 1.59 | 1.54 | 1.64 | 1.67 | 1.67 | 1.53 | 1.62 |
| $PH_3$ | 0.53 | 0.60 | 0.63 | 0.60 | 0.64 | 0.61 | 0.42 | 0.72 | 0.68 | 0.67 | 0.57 |
| Phenol | 1.25 | 1.25 | 1.26 | 1.25 | 1.27 | 1.25 | 1.35 | 1.28 | 1.28 | 1.24 | 1.22 |
| *cis*-Propyleneimine | 1.78 | 1.75 | 1.71 | 1.72 | 1.74 | 1.72 | 1.69 | 1.68 | 1.76 | 1.66 | 1.77 |
| *trans*-Propyleneimine | 1.61 | 1.57 | 1.54 | 1.54 | 1.56 | 1.54 | 1.58 | 1.48 | 1.57 | 1.52 | 1.57 |
| Propyne | 0.86 | 0.88 | 0.87 | 0.87 | 0.90 | 0.87 | 0.87 | 0.84 | 0.87 | 0.87 | 0.78 |
| RbCl | 10.53 | 10.41 | 10.61 | 10.50 | 10.26 | 10.49 | 8.76 | 10.48 | 10.28 | 10.73 | 10.51 |
| RbF | 8.73 | 8.62 | 8.73 | 8.69 | 8.47 | 8.66 | 8.00 | 8.56 | 8.54 | 8.85 | 8.55 |
| ScF | 2.37 | 2.19 | 2.39 | 2.41 | 2.05 | 2.29 | 1.62 | 3.59 | 2.95 | 2.28 | 1.72 |
| ScO | 3.79 | 3.47 | 3.13 | 3.21 | 3.43 | 3.29 | 3.04 | 3.95 | 3.06 | 3.45 | 4.55 |
| $SeO_2$ | 2.75 | 2.65 | 2.66 | 2.62 | 2.61 | 2.62 | 2.64 | 2.69 | 2.75 | 2.68 | 2.62 |
| $SO_2$ | 1.66 | 1.57 | 1.55 | 1.55 | 1.55 | 1.55 | 1.59 | 1.49 | 1.58 | 1.50 | 1.63 |
| SrO | 7.83 | 7.80 | 7.77 | 7.73 | 7.75 | 7.70 | 7.75 | 7.75 | 7.84 | 7.76 | 8.9 |
| TiH | 2.59 | 2.57 | 2.68 | 2.72 | 2.56 | 2.77 | 2.41 | 3.56 | 2.62 | 2.39 | 2.46 |
| TiN | 3.87 | 3.83 | 4.08 | 4.05 | 3.72 | 4.15 | 3.72 | 5.65 | 4.07 | 3.30 | 3.56 |
| TiO | 3.48 | 3.26 | 3.15 | 3.13 | 3.19 | 3.20 | 3.10 | 4.37 | 3.07 | 3.15 | 2.96 |
| TlBr | 4.66 | 4.45 | 4.76 | 4.74 | 4.19 | 4.68 | 4.64 | 4.79 | 4.35 | 4.72 | 4.49 |
| TlCl | 4.67 | 4.46 | 4.76 | 4.71 | 4.19 | 4.66 | 4.60 | 4.76 | 4.46 | 4.81 | 4.54 |
| TlF | 4.22 | 4.05 | 4.21 | 4.20 | 3.86 | 4.16 | 4.23 | 4.27 | 4.15 | 4.24 | 4.23 |
| TlI | 4.50 | 4.31 | 4.64 | 4.64 | 4.05 | 4.58 | 4.68 | 4.67 | 4.11 | 4.50 | 4.61 |
| VN | 3.34 | 3.47 | 4.17 | 3.88 | 3.53 | 3.99 | 3.52 | 5.68 | 3.64 | 3.83 | 3.07 |
| VO | 3.38 | 3.24 | 3.36 | 3.30 | 3.14 | 3.36 | 3.02 | 3.74 | 3.27 | 3.04 | 3.36 |
| YO | 4.71 | 4.38 | 4.04 | 4.15 | 4.34 | 4.20 | 4.35 | 4.02 | 4.22 | 4.25 | 4.52 |
| $ZrO_2$ | 7.45 | 7.39 | 7.34 | 7.34 | 7.36 | 7.33 | 7.24 | 7.15 | 7.44 | 7.37 | 7.80 |
| ZrO | 3.15 | 3.07 | 3.10 | 3.23 | 2.97 | 3.13 | 3.07 | 3.74 | 3.48 | 2.83 | 2.55 |
| MUE (MR)[a] | 0.39 | 0.39 | 0.44 | 0.42 | 0.39 | 0.42 | 0.38 | 0.88 | 0.45 | 0.41 | |
| MUE (SR)[b] | 0.16 | 0.16 | 0.14 | 0.15 | 0.20 | 0.15 | 0.25 | 0.17 | 0.19 | 0.14 | |
| MUE (all)[c] | 0.23 | 0.22 | 0.22 | 0.22 | 0.25 | 0.22 | 0.29 | 0.36 | 0.26 | 0.22 | |
| MSE (all)[d] | −0.03 | −0.07 | −0.03 | −0.04 | −0.11 | −0.04 | −0.15 | 0.17 | −0.05 | −0.06 | |
| General-purpose? | Yes | Yes | Yes | Yes | No | Yes | Yes | No | Yes | Yes | |
| | BLYP | PBE | HCTH/407 | OLYP | PBEsol | OreLYP | SOGGA11 | HLE16 | N12 | GAM | Expt. |

[a] Mean unsigned error calculated over 20 multi-reference molecules. [b] Mean unsigned error calculated over 53 single-reference molecules. [c] Mean unsigned error calculated over all the 73 molecules. [d] Mean signed error calculated over all the 73 molecules.

meta-NGAs are shown in Table 5, those calculated by hybrid GGAs and hybrid NGAs are shown in Tables 6 and 7, and those calculated by hybrid meta-GGAs and hybrid meta-NGAs are shown in Table 8. Some of the functionals were not designed to be general-purpose functionals and this is specified in these tables. For example, at the time that they were published it was stated that M05-2X, M06-2X, M08-HX, and MO8-SO functionals are not parametrized to be suitable for studying many problems in transition metal chemistry or other problems with high multi-reference character due to their high percentage of non-local exchange. The HLE16 and HLE17 functionals, which have high local exchange, were proposed for obtaining improved semiconductor band gaps, but were not proposed as general-purpose gradient approximations like BLYP. PBEsol was proposed as a modified functional especially for solids, with the expectation that it would provide worse atomization energies for solids. Although – simply as a matter of fundamental interest – these functionals are tested here against the same broad datasets as used to test functionals with a general-purpose design, we do indicate next to the mean errors that they are not designed as general-purpose functionals to be sure that the reader does not judge those comparisons as tests of the design strategies for those functionals or for the purposes for which they were designed.

Of the 73 molecules for which MUEs are calculated, 53 are single-reference molecules. In Tables 4–8, overall one finds that for every functional the MUEs over all 53 single-reference molecules are much smaller than the MUEs over the remaining 20 multi-reference molecules, and therefore the MUEs over all the molecules are dominated by large errors in the multi-reference systems. The large errors for multi-reference systems can be attributed to the fact that KS-DFT uses a single configuration state function (in particular a single Slater determinant) as a reference function to represent the density; this, when such a reference function does not provide a good enough description, the density functional would have to work harder. Although we know that a functional that would yield the exact density exists, the currently available functionals do not do as well in such cases. Interestingly, though, there are some molecules that do not have large multi-reference character (according to the $B_1$ diagnostic), but still give large errors for dipole moments; these are AgBr, AgCl, AgI, benzonitrile, CuF,

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Table 5 Dipole moments (in debyes) of 73 molecules using meta-GGAs and meta-NGAs

| Molecule | τ-HCTH | TPSS | M06-L | M11-L | MGGA_MS2 | HLE17 | MN12-L | MN15-L | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| Acetyl chloride | 2.79 | 2.82 | 2.74 | 2.70 | 2.75 | 2.74 | 2.82 | 2.81 | 2.72 |
| AgBr | 5.04 | 4.94 | 5.33 | 6.22 | 4.86 | 5.62 | 5.16 | 5.37 | 5.62 |
| AgCl | 5.26 | 5.16 | 5.70 | 6.15 | 5.12 | 5.86 | 5.37 | 5.61 | 6.08 |
| AgI | 4.56 | 4.45 | 4.67 | 6.03 | 4.36 | 5.07 | 4.61 | 4.65 | 4.55 |
| AlF | 1.37 | 1.35 | 1.31 | 1.31 | 1.26 | 1.33 | 1.30 | 1.21 | 1.53 |
| $AsH_3$ | 0.29 | 0.28 | 0.25 | 0.47 | 0.36 | 0.23 | 0.35 | 0.32 | 0.22 |
| Aziridine | 1.61 | 1.65 | 1.57 | 1.49 | 1.67 | 1.66 | 1.57 | 1.58 | 1.89 |
| Benzonitrile | 4.66 | 4.66 | 4.57 | 4.52 | 4.63 | 4.69 | 4.62 | 4.70 | 4.18 |
| $BF_3NH_3$ | 5.91 | 6.01 | 5.83 | 5.74 | 6.05 | 5.97 | 6.06 | 5.99 | 5.90 |
| $BH_2Cl$ | 0.55 | 0.57 | 0.44 | 0.41 | 0.53 | 0.67 | 0.60 | 0.55 | 0.75 |
| Bromoform | 0.86 | 0.88 | 0.84 | 0.93 | 0.86 | 0.81 | 0.95 | 0.96 | 0.99 |
| Bromomethane | 1.89 | 1.94 | 1.75 | 1.88 | 1.89 | 1.85 | 1.92 | 1.95 | 1.82 |
| $CH_3I$ | 1.71 | 1.73 | 1.51 | 1.86 | 1.70 | 1.55 | 1.70 | 1.66 | 1.64 |
| CrN | 3.24 | 3.07 | 3.06 | 3.14 | 3.02 | 3.42 | 3.24 | 3.28 | 2.31 |
| CrO | 4.26 | 3.73 | 3.99 | 4.08 | 3.62 | 4.48 | 4.44 | 4.25 | 3.88 |
| Dimethyl sulfoxide | 3.78 | 3.82 | 3.72 | 3.45 | 3.88 | 3.91 | 3.77 | 3.80 | 3.96 |
| Ethanol | 1.51 | 1.55 | 1.47 | 1.35 | 1.51 | 1.59 | 1.47 | 1.46 | 1.44 |
| FeO | 4.30 | 4.42 | 4.30 | 4.77 | 4.24 | 5.22 | 4.56 | 4.35 | 4.70 |
| Fluoroacetylene | 0.50 | 0.54 | 0.41 | 0.20 | 0.58 | 0.67 | 0.47 | 0.40 | 0.72 |
| Fluorosilane | 1.21 | 1.25 | 1.18 | 0.92 | 1.20 | 1.28 | 1.02 | 0.99 | 1.27 |
| s-*cis*-Formic acid | 1.52 | 1.49 | 1.52 | 1.54 | 1.51 | 1.60 | 1.62 | 1.59 | 1.43 |
| s-*trans*-Formic acid | 3.78 | 3.80 | 3.72 | 3.70 | 3.80 | 3.93 | 3.92 | 3.87 | 3.79 |
| GeO | 3.13 | 3.13 | 3.29 | 2.86 | 3.06 | 3.48 | 3.13 | 3.22 | 3.28 |
| $H_2CO$ | 2.23 | 2.27 | 2.11 | 2.00 | 2.26 | 2.42 | 2.19 | 2.22 | 2.33 |
| $H_2O$ | 1.88 | 1.87 | 1.85 | 1.85 | 1.84 | 1.87 | 1.91 | 1.87 | 1.85 |
| $H_2S$ | 1.03 | 1.02 | 1.03 | 0.99 | 1.04 | 0.98 | 1.07 | 1.10 | 0.98 |
| HBr | 0.89 | 0.88 | 0.84 | 0.98 | 0.90 | 0.81 | 0.95 | 0.96 | 0.83 |
| HCCI | 0.16 | 0.14 | 0.26 | 0.07 | 0.01 | 0.19 | 0.09 | 0.17 | 0.03 |
| HCl | 1.13 | 1.13 | 1.15 | 1.12 | 1.14 | 1.08 | 1.21 | 1.21 | 1.11 |
| HCN | 2.96 | 2.96 | 2.92 | 2.93 | 2.98 | 2.98 | 3.02 | 3.03 | 2.99 |
| HF | 1.81 | 1.81 | 1.79 | 1.76 | 1.77 | 1.81 | 1.87 | 1.82 | 1.83 |
| $HfO_2$ | 7.55 | 7.68 | 7.92 | 7.79 | 7.78 | 7.95 | 8.36 | 8.10 | 7.92 |
| HfO | 3.44 | 3.47 | 3.13 | 3.20 | 3.32 | 4.41 | 3.49 | 3.45 | 3.43 |
| HI | 0.44 | 0.42 | 0.36 | 0.64 | 0.46 | 0.32 | 0.47 | 0.39 | 0.45 |
| Imidazole | 3.65 | 3.67 | 3.65 | 3.64 | 3.66 | 3.62 | 3.69 | 3.67 | 3.8 |
| Ketene | 1.46 | 1.45 | 1.33 | 1.26 | 1.42 | 1.59 | 1.41 | 1.42 | 1.42 |
| KF | 8.16 | 8.18 | 8.53 | 7.99 | 8.31 | 8.13 | 8.52 | 8.74 | 8.59 |
| LaO | 4.14 | 3.81 | 3.79 | 4.19 | 3.77 | 5.03 | 3.84 | 3.79 | 3.21 |
| LiOH | 4.36 | 4.30 | 4.56 | 4.38 | 4.30 | 4.28 | 4.43 | 4.58 | 4.50 |
| Methylamine | 1.25 | 1.30 | 1.27 | 1.24 | 1.31 | 1.23 | 1.24 | 1.29 | 1.31 |
| Methylphosphine | 1.20 | 1.19 | 1.18 | 1.18 | 1.22 | 1.15 | 1.25 | 1.28 | 1.1 |
| Methylsilane | 0.82 | 0.77 | 0.80 | 0.82 | 0.79 | 0.65 | 0.87 | 0.95 | 0.73 |
| $N_2O$ | 0.13 | 0.09 | 0.16 | 0.17 | 0.00 | 0.01 | 0.05 | 0.03 | 0.16 |
| NaCl | 8.72 | 8.67 | 9.14 | 8.87 | 8.71 | 8.74 | 9.10 | 9.20 | 9.00 |
| $NH_3$ | 1.53 | 1.53 | 1.54 | 1.55 | 1.54 | 1.47 | 1.53 | 1.56 | 1.47 |
| NiH | 2.57 | 2.39 | 2.48 | 2.44 | 2.24 | 2.95 | 2.57 | 2.60 | 2.40 |
| Nitrobenzene | 4.50 | 4.60 | 4.43 | 4.21 | 4.68 | 4.80 | 4.62 | 4.57 | 4.22 |
| Nitromethane | 3.39 | 3.47 | 3.35 | 3.24 | 3.49 | 3.52 | 3.55 | 3.48 | 3.46 |
| Nitrosyl hydride | 1.56 | 1.64 | 1.49 | 1.34 | 1.65 | 1.77 | 1.59 | 1.50 | 1.62 |
| $PH_3$ | 0.62 | 0.63 | 0.63 | 0.56 | 0.66 | 0.65 | 0.64 | 0.65 | 0.57 |
| Phenol | 1.25 | 1.25 | 1.25 | 1.27 | 1.23 | 1.27 | 1.29 | 1.25 | 1.22 |
| *cis*-Propyleneimine | 1.72 | 1.76 | 1.69 | 1.58 | 1.77 | 1.77 | 1.67 | 1.67 | 1.77 |
| *trans*-Propyleneimine | 1.55 | 1.60 | 1.53 | 1.45 | 1.61 | 1.60 | 1.53 | 1.55 | 1.57 |
| Propyne | 0.85 | 0.84 | 0.84 | 0.83 | 0.79 | 0.74 | 0.84 | 0.85 | 0.78 |
| RbCl | 10.55 | 10.58 | 11.12 | 10.83 | 10.79 | 10.64 | 11.13 | 11.35 | 10.51 |
| RbF | 8.65 | 8.71 | 9.16 | 8.70 | 8.88 | 8.74 | 9.11 | 9.26 | 8.55 |
| ScF | 2.30 | 2.33 | 2.29 | 1.91 | 2.14 | 3.98 | 2.48 | 2.32 | 1.72 |
| ScO | 3.23 | 3.42 | 3.65 | 3.59 | 3.40 | 4.31 | 3.75 | 3.82 | 4.55 |
| $SeO_2$ | 2.63 | 2.63 | 2.69 | 2.54 | 2.60 | 2.83 | 2.67 | 2.62 | 2.62 |
| $SO_2$ | 1.56 | 1.57 | 1.49 | 1.44 | 1.56 | 1.62 | 1.50 | 1.50 | 1.63 |
| SrO | 7.93 | 8.06 | 8.33 | 8.02 | 8.17 | 8.50 | 8.20 | 8.23 | 8.9 |
| TiH | 2.92 | 2.58 | 3.64 | 3.04 | 2.49 | 3.30 | 2.41 | 3.29 | 2.46 |
| TiN | 4.73 | 4.26 | 4.49 | 4.63 | 3.97 | 6.26 | 5.44 | 4.27 | 3.56 |
| TiO | 3.62 | 3.37 | 3.39 | 3.15 | 3.32 | 3.71 | 3.19 | 3.39 | 2.96 |
| TlBr | 4.70 | 4.59 | 4.77 | 4.67 | 4.25 | 5.00 | 4.41 | 4.87 | 4.49 |
| TlCl | 4.64 | 4.55 | 4.80 | 4.35 | 4.24 | 4.97 | 4.34 | 4.81 | 4.54 |
| TlF | 4.06 | 4.00 | 4.15 | 3.40 | 3.75 | 4.34 | 3.67 | 4.08 | 4.23 |
| TlI | 4.63 | 4.49 | 4.46 | 4.92 | 4.11 | 4.87 | 4.25 | 4.60 | 4.61 |
| VN | 4.74 | 3.42 | 4.12 | 3.22 | 3.08 | 5.10 | 3.54 | 4.08 | 3.07 |
| VO | 3.86 | 3.48 | 3.32 | 4.02 | 3.44 | 4.11 | 4.77 | 3.65 | 3.36 |

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Table 5 (*continued*)

| Molecule | τ-HCTH | TPSS | M06-L | M11-L | MGGA_MS2 | HLE17 | MN12-L | MN15-L | Expt. |
|---|---|---|---|---|---|---|---|---|---|
| YO | 3.84 | 4.36 | 4.43 | 3.82 | 4.38 | 4.23 | 4.16 | 4.58 | 4.52 |
| $ZrO_2$ | 7.42 | 7.60 | 7.83 | 7.64 | 7.73 | 7.61 | 8.22 | 8.00 | 7.80 |
| ZrO | 3.01 | 3.33 | 2.90 | 2.87 | 3.24 | 4.36 | 2.99 | 3.05 | 2.55 |
| MUE (MR)[a] | 0.58 | 0.38 | 0.37 | 0.42 | 0.34 | 0.85 | 0.53 | 0.40 | |
| MUE (SR)[b] | 0.14 | 0.13 | 0.17 | 0.22 | 0.16 | 0.16 | 0.17 | 0.18 | |
| MUE (all)[c] | 0.26 | 0.20 | 0.22 | 0.28 | 0.21 | 0.35 | 0.27 | 0.24 | |
| MSE (all)[d] | 0.02 | −0.01 | 0.04 | 0.00 | −0.05 | 0.25 | 0.08 | 0.10 | |
| General-purpose? | Yes | Yes | Yes | Yes | Yes | No | Yes | Yes | |
| | τ-HCTH | TPSS | M06-L | M11-L | MGGA_MS2 | HLE17 | MN12-L | MN15-L | Expt. |

[a] Mean unsigned error calculated over 20 multi-reference molecules. [b] Mean unsigned error calculated over 53 single-reference molecules. [c] Mean unsigned error calculated over all the 73 molecules. [d] Mean signed error calculated over all the 73 molecules.

Table 6 Dipole moments (in debyes) of 73 molecules using hybrid GGAs published in 2001 or earlier

| Molecule | BHandHLYP | B3LYP | B3LYP-D3(BJ) | B1LYP | mPW1PW | B97-1 | PBE0 | MPW1K | B3LYP* | Expt. |
|---|---|---|---|---|---|---|---|---|---|---|
| Acetyl chloride | 2.87 | 2.85 | 2.85 | 2.86 | 2.81 | 2.85 | 2.80 | 2.83 | 2.85 | 2.72 |
| AgBr | 6.02 | 5.18 | 5.18 | 5.33 | 5.43 | 5.33 | 5.42 | 5.92 | 5.00 | 5.62 |
| AgCl | 6.20 | 5.43 | 5.43 | 5.57 | 5.63 | 5.55 | 5.62 | 6.08 | 5.26 | 6.08 |
| AgI | 5.56 | 4.64 | 4.64 | 4.80 | 4.96 | 4.83 | 4.95 | 5.50 | 4.46 | 4.55 |
| AlF | 1.48 | 1.56 | 1.56 | 1.56 | 1.42 | 1.47 | 1.43 | 1.36 | 1.57 | 1.53 |
| $AsH_3$ | 0.35 | 0.25 | 0.25 | 0.26 | 0.35 | 0.30 | 0.36 | 0.41 | 0.25 | 0.22 |
| Aziridine | 1.72 | 1.69 | 1.69 | 1.70 | 1.67 | 1.68 | 1.66 | 1.69 | 1.68 | 1.89 |
| Benzonitrile | 4.79 | 4.71 | 4.71 | 4.72 | 4.71 | 4.71 | 4.70 | 4.75 | 4.70 | 4.18 |
| $BF_3NH_3$ | 6.15 | 6.08 | 6.07 | 6.08 | 6.10 | 6.09 | 6.10 | 6.14 | 6.07 | 5.90 |
| $BH_2Cl$ | 0.75 | 0.61 | 0.61 | 0.64 | 0.59 | 0.62 | 0.57 | 0.67 | 0.57 | 0.75 |
| Bromoform | 0.92 | 0.88 | 0.88 | 0.89 | 0.89 | 0.89 | 0.89 | 0.91 | 0.88 | 0.99 |
| Bromomethane | 2.00 | 1.93 | 1.93 | 1.95 | 1.91 | 1.93 | 1.91 | 1.95 | 1.92 | 1.82 |
| $CH_3I$ | 1.77 | 1.70 | 1.70 | 1.71 | 1.71 | 1.70 | 1.71 | 1.75 | 1.69 | 1.64 |
| CrN | 3.58 | 3.16 | 3.16 | 3.21 | 3.10 | 3.15 | 3.10 | 3.34 | 3.11 | 2.31 |
| CrO | 4.43 | 4.15 | 4.15 | 4.27 | 4.15 | 4.25 | 4.13 | 4.47 | 4.01 | 3.88 |
| Dimethyl sulfoxide | 4.17 | 3.99 | 3.99 | 4.02 | 3.98 | 3.94 | 3.98 | 4.09 | 3.95 | 3.96 |
| Ethanol | 1.61 | 1.58 | 1.58 | 1.59 | 1.55 | 1.56 | 1.55 | 1.57 | 1.57 | 1.44 |
| FeO | 5.71 | 5.17 | 5.17 | 5.37 | 5.28 | 5.45 | 5.28 | 5.76 | 4.95 | 4.70 |
| Fluoroacetylene | 0.70 | 0.62 | 0.62 | 0.64 | 0.58 | 0.57 | 0.56 | 0.62 | 0.60 | 0.72 |
| Fluorosilane | 1.33 | 1.32 | 1.32 | 1.32 | 1.27 | 1.28 | 1.27 | 1.28 | 1.31 | 1.27 |
| s-*cis*-Formic acid | 1.62 | 1.54 | 1.54 | 1.55 | 1.57 | 1.55 | 1.57 | 1.61 | 1.53 | 1.43 |
| s-*trans*-Formic acid | 4.10 | 3.92 | 3.92 | 3.95 | 3.94 | 3.92 | 3.94 | 4.04 | 3.90 | 3.79 |
| GeO | 3.71 | 3.46 | 3.46 | 3.51 | 3.39 | 3.41 | 3.39 | 3.54 | 3.40 | 3.28 |
| $H_2CO$ | 2.51 | 2.36 | 2.36 | 2.39 | 2.35 | 2.35 | 2.34 | 2.44 | 2.34 | 2.33 |
| $H_2O$ | 1.94 | 1.91 | 1.91 | 1.91 | 1.91 | 1.90 | 1.91 | 1.93 | 1.90 | 1.85 |
| $H_2S$ | 1.05 | 1.02 | 1.02 | 1.02 | 1.05 | 1.03 | 1.06 | 1.08 | 1.01 | 0.98 |
| HBr | 0.93 | 0.89 | 0.89 | 0.89 | 0.92 | 0.90 | 0.92 | 0.94 | 0.89 | 0.83 |
| HCCI | 0.01 | 0.14 | 0.14 | 0.12 | 0.07 | 0.14 | 0.07 | 0.02 | 0.16 | 0.03 |
| HCl | 1.16 | 1.14 | 1.14 | 1.14 | 1.15 | 1.15 | 1.16 | 1.17 | 1.14 | 1.11 |
| HCN | 3.13 | 3.03 | 3.03 | 3.05 | 3.04 | 3.03 | 3.04 | 3.10 | 3.02 | 2.99 |
| HF | 1.87 | 1.84 | 1.84 | 1.84 | 1.84 | 1.82 | 1.83 | 1.85 | 1.84 | 1.83 |
| $HfO_2$ | 8.59 | 7.99 | 7.99 | 8.10 | 8.10 | 8.01 | 8.07 | 8.44 | 7.86 | 7.92 |
| HfO | 3.75 | 3.55 | 3.55 | 3.59 | 3.43 | 3.43 | 3.39 | 3.52 | 3.50 | 3.43 |
| HI | 0.48 | 0.43 | 0.43 | 0.44 | 0.47 | 0.44 | 0.48 | 0.51 | 0.43 | 0.45 |
| Imidazole | 3.77 | 3.72 | 3.72 | 3.73 | 3.74 | 3.72 | 3.74 | 3.77 | 3.72 | 3.8 |
| Ketene | 1.52 | 1.49 | 1.49 | 1.49 | 1.47 | 1.47 | 1.47 | 1.49 | 1.49 | 1.42 |
| KF | 8.62 | 8.43 | 8.43 | 8.48 | 8.41 | 8.46 | 8.39 | 8.52 | 8.36 | 8.59 |
| LaO | 4.21 | 4.25 | 4.25 | 4.27 | 3.87 | 3.91 | 3.84 | 3.79 | 4.24 | 3.21 |
| LiOH | 4.41 | 4.34 | 4.33 | 4.35 | 4.40 | 4.40 | 4.38 | 4.45 | 4.31 | 4.50 |
| Methylamine | 1.30 | 1.29 | 1.29 | 1.29 | 1.29 | 1.30 | 1.29 | 1.29 | 1.28 | 1.31 |
| Methylphosphine | 1.20 | 1.15 | 1.15 | 1.15 | 1.22 | 1.18 | 1.23 | 1.26 | 1.15 | 1.1 |
| Methylsilane | 0.75 | 0.78 | 0.77 | 0.77 | 0.82 | 0.79 | 0.82 | 0.81 | 0.79 | 0.73 |
| $N_2O$ | 0.29 | 0.07 | 0.07 | 0.11 | 0.04 | 0.06 | 0.03 | 0.17 | 0.02 | 0.16 |
| NaCl | 8.91 | 8.71 | 8.71 | 8.73 | 8.84 | 8.82 | 8.80 | 8.97 | 8.65 | 9.00 |
| $NH_3$ | 1.54 | 1.53 | 1.53 | 1.53 | 1.55 | 1.55 | 1.55 | 1.55 | 1.53 | 1.47 |
| NiH | 3.04 | 2.46 | 2.47 | 2.55 | 2.68 | 2.59 | 2.66 | 3.05 | 2.36 | 2.40 |
| Nitrobenzene | 4.77 | 4.69 | 4.69 | 4.71 | 4.58 | 4.65 | 4.57 | 4.63 | 4.67 | 4.22 |
| Nitromethane | 3.74 | 3.59 | 3.59 | 3.62 | 3.55 | 3.57 | 3.55 | 3.64 | 3.57 | 3.46 |

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Table 6 (*continued*)

| Molecule | BHandHLYP | B3LYP | B3LYP-D3(BJ) | B1LYP | mPW1PW | B97-1 | PBE0 | MPW1K | B3LYP* | Expt. |
|---|---|---|---|---|---|---|---|---|---|---|
| Nitrosyl hydride | 1.82 | 1.71 | 1.71 | 1.73 | 1.72 | 1.68 | 1.71 | 1.78 | 1.69 | 1.62 |
| $PH_3$ | 0.65 | 0.59 | 0.59 | 0.59 | 0.65 | 0.62 | 0.66 | 0.69 | 0.58 | 0.57 |
| Phenol | 1.31 | 1.28 | 1.28 | 1.28 | 1.28 | 1.27 | 1.28 | 1.30 | 1.28 | 1.22 |
| *cis*-Propyleneimine | 1.84 | 1.81 | 1.81 | 1.81 | 1.78 | 1.80 | 1.78 | 1.80 | 1.80 | 1.77 |
| *trans*-Propyleneimine | 1.67 | 1.63 | 1.64 | 1.64 | 1.61 | 1.63 | 1.60 | 1.63 | 1.62 | 1.57 |
| Propyne | 0.81 | 0.84 | 0.84 | 0.83 | 0.84 | 0.85 | 0.85 | 0.83 | 0.85 | 0.78 |
| RbCl | 11.03 | 10.78 | 10.78 | 10.84 | 10.75 | 10.79 | 10.72 | 10.88 | 10.69 | 10.51 |
| RbF | 9.13 | 8.94 | 8.94 | 9.00 | 8.91 | 8.96 | 8.89 | 9.02 | 8.87 | 8.55 |
| ScF | 2.70 | 2.57 | 2.57 | 2.61 | 2.51 | 2.34 | 2.42 | 2.30 | 2.49 | 1.72 |
| ScO | 4.13 | 3.92 | 3.92 | 3.97 | 3.63 | 3.48 | 3.61 | 3.72 | 3.87 | 4.55 |
| $SeO_2$ | 3.05 | 2.88 | 2.88 | 2.92 | 2.82 | 2.82 | 2.81 | 2.91 | 2.85 | 2.62 |
| $SO_2$ | 1.79 | 1.71 | 1.71 | 1.73 | 1.66 | 1.66 | 1.65 | 1.70 | 1.69 | 1.63 |
| SrO | 9.62 | 8.67 | 8.67 | 8.85 | 8.80 | 8.68 | 8.75 | 9.31 | 8.47 | 8.9 |
| TiH | 2.63 | 2.73 | 2.74 | 2.73 | 2.74 | 2.63 | 2.72 | 2.68 | 2.70 | 2.46 |
| TiN | 3.46 | 3.50 | 3.50 | 3.51 | 3.30 | 3.45 | 3.28 | 3.25 | 3.49 | 3.56 |
| TiO | 3.90 | 3.65 | 3.65 | 3.71 | 3.48 | 3.37 | 3.45 | 3.58 | 3.59 | 2.96 |
| TlBr | 4.91 | 4.77 | 4.77 | 4.82 | 4.64 | 4.74 | 4.61 | 4.70 | 4.69 | 4.49 |
| TlCl | 4.83 | 4.74 | 4.74 | 4.79 | 4.59 | 4.72 | 4.56 | 4.62 | 4.67 | 4.54 |
| TlF | 4.31 | 4.27 | 4.27 | 4.30 | 4.14 | 4.25 | 4.13 | 4.15 | 4.23 | 4.23 |
| TlI | 4.85 | 4.65 | 4.65 | 4.72 | 4.55 | 4.64 | 4.52 | 4.64 | 4.56 | 4.61 |
| VN | 3.21 | 3.23 | 3.23 | 3.24 | 3.08 | 3.10 | 3.07 | 3.05 | 3.21 | 3.07 |
| VO | 3.97 | 3.64 | 3.64 | 3.71 | 3.56 | 3.57 | 3.53 | 3.72 | 3.55 | 3.36 |
| YO | 4.97 | 4.83 | 4.83 | 4.87 | 4.51 | 4.45 | 4.48 | 4.55 | 4.79 | 4.52 |
| $ZrO_2$ | 8.28 | 7.83 | 7.83 | 7.91 | 7.87 | 7.83 | 7.85 | 8.13 | 7.73 | 7.80 |
| ZrO | 3.54 | 3.32 | 3.32 | 3.37 | 3.37 | 3.01 | 3.30 | 3.51 | 3.25 | 2.55 |
| MUE (MR)[a] | 0.59 | 0.37 | 0.37 | 0.41 | 0.33 | 0.32 | 0.32 | 0.45 | 0.34 | |
| MUE (SR)[b] | 0.19 | 0.13 | 0.13 | 0.14 | 0.13 | 0.13 | 0.13 | 0.16 | 0.13 | |
| MUE (all)[c] | 0.30 | 0.20 | 0.20 | 0.21 | 0.19 | 0.18 | 0.18 | 0.24 | 0.19 | |
| MSE (all)[d] | 0.27 | 0.11 | 0.11 | 0.14 | 0.09 | 0.08 | 0.08 | 0.18 | 0.06 | |
| General-purpose? | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes | |
| | BHandHLYP | B3LYP | B3LYP-D3(BJ) | B1LYP | mPW1PW | B97-1 | PBE0 | MPW1K | B3LYP* | Expt. |

[a] Mean unsigned error calculated over 20 multi-reference molecules. [b] Mean unsigned error calculated over 53 single-reference molecules. [c] Mean unsigned error calculated over all the 73 molecules. [d] Mean signed error calculated over all the 73 molecules.

NiH, nitrobenzene, PbS, RbCl, RbF, and TiH whose average error with the 47 functionals (excluding B3LYP-D3(BJ)) are 0.44, 0.52, 0.51, 0.50, 0.62, 0.34, 0.38, 0.59, 0.33, 0.38, and 0.37 D, respectively.

If we look at trends for individual molecules in Tables 4–8, we see that the experimental dipole moments of formic acid in *cis* and *trans* forms are 1.43 and 3.79 D, respectively, and all the functionals also predict that formic acid in *cis* form has smaller dipole moment than formic acid in *trans* form. Similarly for propyleneimine the experimental dipole moments in *cis* and *trans* forms are 1.77 and 1.57 D, respectively, and the same order is predicted by all the functionals. For oxides of hafnium and zirconium, the more oxidized forms ($HfO_2$ and $ZrO_2$ as compared to HfO and ZrO) have larger dipole moments and the theoretically calculated values with all the functionals also show the same trend. Next we analyze the performance of the functionals based on their type.

Table 4 gives the performance of eight GGAs (PBE, BLYP, OLYP, OreLYP, PBEsol, SOGGA11, HCTH/407 and HLE16) and two NGAs (N12 and GAM). For single-reference systems all functionals except SOGGA11 give MUEs less than or equal to 0.20 D, and all functionals also show similar performances for multi-reference systems except for that of HLE16 that has a large MUE (0.88 D). The HLE16 functional is a recently developed functional that has more local exchange than a typical local functional and which was found to be good for band gaps and excitation energies, but it is clearly not good for multi-reference systems. The GAM functional, which was obtained by reoptimizing N12 with smoothness constraints and on a database broader than N12, shows slightly better performance than N12 on both single-reference and multi-reference systems. In summary, based on overall MUE, we can say that the best performing functionals in this category are PBE, HCTH/407, OLYP, OreLYP and GAM – all have MUEs equal to 0.22 D; the next best performing functional, BLYP, is very close to this value.

Table 5 presents results for six meta-GGAs (τ-HCTH, TPSS, M06-L, M11-L, MGGA_MS2 and HLE17) and two meta-NGAs (MN12-L and MN15-L). The performances of these eight functionals are all quite similar to each other for single-reference systems, and the MUEs are less than 0.20 D (except that M11-L has an MUE of 0.22 D), while for multi-reference systems all these functionals give MUEs greater than or equal to 0.34 D besides also giving a greater spread in the values. The recently developed HLE17 functional, which is similar to HLE16 in having high local exchange, gives a large MUE (0.85 D) for

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Table 7 Dipole moments (in debyes) of 73 molecules using six hybrid GGAs published from 2004 to 2011 and a hybrid NGA

| Molecule | CAM-B3LYP | MPW3LYP | B97-3 | LC-ωPBE | HSE06 | SOGGA11-X | N12-SX | Expt. |
|---|---|---|---|---|---|---|---|---|
| Acetyl chloride | 2.84 | 2.85 | 2.84 | 2.79 | 2.81 | 2.82 | 2.86 | 2.72 |
| AgBr | 5.58 | 5.19 | 5.60 | 6.05 | 5.35 | 5.72 | 5.25 | 5.62 |
| AgCl | 5.77 | 5.44 | 5.78 | 6.16 | 5.57 | 5.92 | 5.48 | 6.08 |
| AgI | 5.11 | 4.65 | 5.09 | 5.70 | 4.86 | 5.21 | 4.73 | 4.55 |
| AlF | 1.51 | 1.57 | 1.46 | 1.31 | 1.45 | 1.42 | 1.35 | 1.53 |
| $AsH_3$ | 0.34 | 0.26 | 0.32 | 0.48 | 0.34 | 0.35 | 0.36 | 0.22 |
| Aziridine | 1.73 | 1.69 | 1.68 | 1.73 | 1.66 | 1.67 | 1.69 | 1.89 |
| Benzonitrile | 4.72 | 4.71 | 4.71 | 4.70 | 4.70 | 4.73 | 4.76 | 4.18 |
| $BF_3NH_3$ | 6.15 | 6.08 | 6.12 | 6.22 | 6.10 | 6.13 | 6.16 | 5.90 |
| $BH_2Cl$ | 0.64 | 0.61 | 0.62 | 0.64 | 0.58 | 0.66 | 0.66 | 0.75 |
| Bromoform | 0.90 | 0.88 | 0.90 | 0.91 | 0.88 | 0.92 | 0.89 | 0.99 |
| Bromomethane | 1.92 | 1.93 | 1.93 | 1.88 | 1.91 | 1.94 | 1.92 | 1.82 |
| $CH_3I$ | 1.68 | 1.69 | 1.70 | 1.65 | 1.71 | 1.72 | 1.68 | 1.64 |
| CrN | 3.17 | 3.17 | 3.13 | 2.95 | 3.08 | 3.09 | 3.31 | 2.31 |
| CrO | 4.38 | 4.19 | 4.26 | 4.42 | 4.09 | 4.59 | 4.37 | 3.88 |
| Dimethyl sulfoxide | 4.12 | 3.99 | 4.01 | 4.16 | 3.98 | 4.06 | 4.08 | 3.96 |
| Ethanol | 1.61 | 1.58 | 1.57 | 1.62 | 1.55 | 1.56 | 1.59 | 1.44 |
| FeO | 5.55 | 5.23 | 5.57 | 5.58 | 5.22 | 5.99 | 5.28 | 4.70 |
| Fluoroacetylene | 0.67 | 0.62 | 0.58 | 0.67 | 0.57 | 0.62 | 0.66 | 0.72 |
| Fluorosilane | 1.33 | 1.32 | 1.29 | 1.32 | 1.28 | 1.31 | 1.31 | 1.27 |
| s-*cis*-Formic acid | 1.56 | 1.54 | 1.57 | 1.57 | 1.56 | 1.59 | 1.61 | 1.43 |
| s-*trans*-Formic acid | 4.02 | 3.94 | 3.95 | 4.04 | 3.93 | 3.99 | 4.03 | 3.79 |
| GeO | 3.55 | 3.47 | 3.50 | 3.48 | 3.40 | 3.56 | 3.47 | 3.28 |
| $H_2CO$ | 2.44 | 2.37 | 2.37 | 2.45 | 2.35 | 2.41 | 2.42 | 2.33 |
| $H_2O$ | 1.94 | 1.91 | 1.90 | 1.95 | 1.91 | 1.90 | 1.95 | 1.85 |
| $H_2S$ | 1.06 | 1.02 | 1.05 | 1.12 | 1.05 | 1.06 | 1.09 | 0.98 |
| HBr | 0.93 | 0.90 | 0.91 | 0.95 | 0.92 | 0.93 | 0.92 | 0.83 |
| HCCI | 0.04 | 0.14 | 0.09 | 0.08 | 0.08 | 0.03 | 0.11 | 0.03 |
| HCl | 1.17 | 1.14 | 1.15 | 1.19 | 1.15 | 1.16 | 1.17 | 1.11 |
| HCN | 3.09 | 3.04 | 3.04 | 3.10 | 3.04 | 3.07 | 3.07 | 2.99 |
| HF | 1.86 | 1.85 | 1.83 | 1.86 | 1.84 | 1.83 | 1.88 | 1.83 |
| $HfO_2$ | 8.35 | 8.02 | 8.11 | 8.59 | 8.06 | 8.36 | 8.13 | 7.92 |
| HfO | 3.69 | 3.57 | 3.42 | 3.56 | 3.42 | 3.50 | 3.54 | 3.43 |
| HI | 0.47 | 0.44 | 0.45 | 0.51 | 0.47 | 0.46 | 0.46 | 0.45 |
| Imidazole | 3.79 | 3.73 | 3.74 | 3.84 | 3.74 | 3.74 | 3.74 | 3.8 |
| Ketene | 1.50 | 1.49 | 1.47 | 1.45 | 1.47 | 1.47 | 1.57 | 1.42 |
| KF | 8.49 | 8.40 | 8.61 | 8.61 | 8.39 | 8.59 | 8.43 | 8.59 |
| LaO | 4.22 | 4.27 | 3.89 | 3.51 | 3.94 | 3.92 | 3.67 | 3.21 |
| LiOH | 4.33 | 4.30 | 4.48 | 4.43 | 4.38 | 4.48 | 4.39 | 4.50 |
| Methylamine | 1.30 | 1.28 | 1.30 | 1.32 | 1.28 | 1.31 | 1.24 | 1.31 |
| Methylphosphine | 1.19 | 1.15 | 1.20 | 1.29 | 1.22 | 1.23 | 1.27 | 1.1 |
| Methylsilane | 0.77 | 0.77 | 0.80 | 0.81 | 0.82 | 0.78 | 0.81 | 0.73 |
| $N_2O$ | 0.16 | 0.08 | 0.08 | 0.16 | 0.03 | 0.17 | 0.10 | 0.16 |
| NaCl | 8.78 | 8.63 | 8.99 | 9.00 | 8.80 | 8.97 | 8.86 | 9.00 |
| $NH_3$ | 1.54 | 1.53 | 1.55 | 1.56 | 1.55 | 1.56 | 1.52 | 1.47 |
| NiH | 2.72 | 2.48 | 2.69 | 3.15 | 2.61 | 2.78 | 2.58 | 2.40 |
| Nitrobenzene | 4.65 | 4.69 | 4.64 | 4.50 | 4.58 | 4.62 | 4.73 | 4.22 |
| Nitromethane | 3.67 | 3.60 | 3.59 | 3.65 | 3.55 | 3.62 | 3.64 | 3.46 |
| Nitrosyl hydride | 1.78 | 1.72 | 1.69 | 1.80 | 1.71 | 1.71 | 1.79 | 1.62 |
| $PH_3$ | 0.64 | 0.59 | 0.64 | 0.75 | 0.65 | 0.66 | 0.71 | 0.57 |
| Phenol | 1.31 | 1.28 | 1.28 | 1.32 | 1.28 | 1.27 | 1.31 | 1.22 |
| *cis*-Propyleneimine | 1.84 | 1.81 | 1.80 | 1.85 | 1.78 | 1.78 | 1.81 | 1.77 |
| *trans*-Propyleneimine | 1.67 | 1.64 | 1.63 | 1.67 | 1.60 | 1.61 | 1.63 | 1.57 |
| Propyne | 0.82 | 0.84 | 0.84 | 0.80 | 0.85 | 0.82 | 0.85 | 0.78 |
| RbCl | 10.91 | 10.72 | 11.02 | 11.02 | 10.71 | 11.02 | 10.71 | 10.51 |
| RbF | 9.03 | 8.91 | 9.13 | 9.16 | 8.89 | 9.15 | 8.90 | 8.55 |
| ScF | 2.65 | 2.58 | 2.48 | 2.04 | 2.45 | 2.35 | 2.43 | 1.72 |
| ScO | 3.95 | 3.95 | 3.62 | 3.35 | 3.71 | 3.66 | 3.08 | 4.55 |
| $SeO_2$ | 2.98 | 2.90 | 2.85 | 2.94 | 2.82 | 2.89 | 2.93 | 2.62 |
| $SO_2$ | 1.75 | 1.72 | 1.67 | 1.70 | 1.65 | 1.68 | 1.69 | 1.63 |
| SrO | 9.39 | 8.72 | 8.85 | 9.76 | 8.72 | 9.41 | 8.75 | 8.9 |
| TiH | 2.80 | 2.72 | 2.49 | 2.88 | 2.72 | 2.74 | 2.78 | 2.46 |
| TiN | 3.44 | 3.51 | 3.30 | 3.00 | 3.35 | 3.19 | 4.30 | 3.56 |
| TiO | 3.70 | 3.68 | 3.43 | 3.30 | 3.52 | 3.59 | 3.12 | 2.96 |
| TlBr | 4.75 | 4.73 | 4.92 | 4.66 | 4.59 | 4.78 | 4.58 | 4.49 |
| TlCl | 4.69 | 4.71 | 4.84 | 4.56 | 4.56 | 4.73 | 4.58 | 4.54 |
| TlF | 4.20 | 4.26 | 4.34 | 4.05 | 4.14 | 4.29 | 4.22 | 4.23 |
| TlI | 4.69 | 4.62 | 4.80 | 4.66 | 4.48 | 4.64 | 4.41 | 4.61 |
| VN | 3.18 | 3.24 | 3.09 | 3.25 | 3.11 | 2.98 | 3.43 | 3.07 |
| VO | 3.73 | 3.66 | 3.55 | 3.56 | 3.53 | 3.74 | 3.84 | 3.36 |

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Table 7 (*continued*)

| Molecule | CAM-B3LYP | MPW3LYP | B97-3 | LC-ωPBE | HSE06 | SOGGA11-X | N12-SX | Expt. |
|---|---|---|---|---|---|---|---|---|
| YO | 4.91 | 4.85 | 4.50 | 4.38 | 4.58 | 4.62 | 4.18 | 4.52 |
| $ZrO_2$ | 8.08 | 7.85 | 7.91 | 8.21 | 7.85 | 8.09 | 7.92 | 7.80 |
| ZrO | 3.38 | 3.32 | 3.21 | 3.52 | 3.27 | 2.88 | 3.01 | 2.55 |
| MUE (MR)[a] | 0.48 | 0.38 | 0.35 | 0.45 | 0.32 | 0.44 | 0.42 | |
| MUE (SR)[b] | 0.15 | 0.13 | 0.14 | 0.18 | 0.13 | 0.14 | 0.15 | |
| MUE (all)[c] | 0.24 | 0.20 | 0.20 | 0.25 | 0.18 | 0.22 | 0.23 | |
| MSE (all)[d] | 0.18 | 0.11 | 0.13 | 0.18 | 0.08 | 0.16 | 0.11 | |
| General-purpose? | Yes | Yes | Yes | Yes | Yes | Yes | Yes | |
| | CAM-B3LYP | MPW3LYP | B97-3 | LC-ωPBE | HSE06 | SOGGA11-X | N12-SX | Expt. |

[a] Mean unsigned error calculated over 20 multi-reference molecules. [b] Mean unsigned error calculated over 53 single-reference molecules. [c] Mean unsigned error calculated over all the 73 molecules. [d] Mean signed error calculated over all the 73 molecules.

Table 8 Dipole moments (in debyes) of 73 molecules using hybrid meta-GGAs and hybrid meta-NGAs

| Molecule | τ-HCTHhyb | TPSSh | MPWB1K | M05 | M05-2X | PW6B95 | M06-HF | M06 | M06-2X | M08-HX | M08-SO | M11 | MN12-SX | MN15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Acetyl chloride | 2.84 | 2.81 | 2.81 | 2.82 | 2.88 | 2.80 | 2.92 | 2.77 | 2.82 | 2.80 | 2.81 | 2.91 | 2.79 | 2.80 |
| AgBr | 5.11 | 5.23 | 5.81 | 5.63 | 6.05 | 5.38 | 6.50 | 5.32 | 6.09 | 6.31 | 5.82 | 6.31 | 5.63 | 5.42 |
| AgCl | 5.35 | 5.43 | 6.00 | 5.88 | 6.13 | 5.62 | 6.49 | 5.60 | 6.25 | 6.40 | 6.04 | 6.41 | 5.78 | 5.65 |
| AgI | 4.61 | 4.75 | 5.35 | 4.96 | 5.74 | 4.86 | 6.43 | 4.60 | 5.70 | 6.06 | 5.24 | 6.02 | 5.15 | 4.76 |
| AlF | 1.45 | 1.34 | 1.46 | 1.46 | 1.65 | 1.55 | 1.85 | 1.50 | 1.58 | 1.53 | 1.63 | 1.43 | 1.67 | 1.52 |
| $AsH_3$ | 0.29 | 0.32 | 0.36 | 0.32 | 0.43 | 0.27 | 0.37 | 0.24 | 0.37 | 0.33 | 0.27 | 0.27 | 0.31 | 0.35 |
| Aziridine | 1.67 | 1.66 | 1.68 | 1.64 | 1.76 | 1.67 | 1.80 | 1.62 | 1.69 | 1.68 | 1.68 | 1.74 | 1.60 | 1.67 |
| Benzonitrile | 4.70 | 4.69 | 4.71 | 4.72 | 4.79 | 4.67 | 4.83 | 4.62 | 4.67 | 4.64 | 4.66 | 4.77 | 4.60 | 4.65 |
| $BF_3NH_3$ | 6.05 | 6.05 | 6.10 | 5.82 | 6.14 | 6.06 | 6.31 | 5.85 | 6.07 | 6.20 | 6.08 | 6.23 | 6.09 | 6.06 |
| $BH_2Cl$ | 0.60 | 0.61 | 0.62 | 0.62 | 0.78 | 0.57 | 1.02 | 0.52 | 0.71 | 0.69 | 0.69 | 0.74 | 0.64 | 0.58 |
| Bromoform | 0.88 | 0.89 | 0.90 | 0.84 | 0.96 | 0.88 | 0.97 | 0.84 | 0.91 | 0.92 | 0.90 | 0.95 | 0.91 | 0.94 |
| Bromomethane | 1.92 | 1.95 | 1.92 | 1.83 | 2.06 | 1.89 | 2.17 | 1.77 | 1.93 | 1.97 | 1.90 | 2.01 | 1.88 | 1.93 |
| $CH_3I$ | 1.71 | 1.75 | 1.71 | 1.54 | 1.88 | 1.66 | 2.10 | 1.48 | 1.70 | 1.76 | 1.62 | 1.82 | 1.67 | 1.63 |
| CrN | 3.16 | 3.12 | 3.12 | 2.92 | 3.20 | 3.06 | 3.76 | 3.01 | 3.23 | 3.11 | 4.01 | 3.01 | 4.11 | 3.06 |
| CrO | 4.26 | 3.97 | 4.47 | 4.62 | 4.98 | 4.22 | 5.19 | 4.62 | 4.51 | 4.99 | 4.92 | 4.77 | 5.14 | 4.52 |
| Dimethyl sulfoxide | 3.91 | 3.89 | 4.07 | 3.86 | 4.26 | 3.98 | 4.54 | 3.85 | 4.12 | 4.13 | 4.13 | 4.21 | 3.86 | 4.09 |
| Ethanol | 1.55 | 1.56 | 1.57 | 1.55 | 1.65 | 1.56 | 1.72 | 1.52 | 1.59 | 1.58 | 1.59 | 1.64 | 1.50 | 1.58 |
| FeO | 5.30 | 4.83 | 5.94 | 4.47 | 7.00 | 5.42 | 7.42 | 5.64 | 6.22 | 6.96 | 6.51 | 6.72 | 6.01 | 5.58 |
| Fluoroacetylene | 0.56 | 0.57 | 0.65 | 0.55 | 0.74 | 0.63 | 0.98 | 0.54 | 0.71 | 0.71 | 0.75 | 0.75 | 0.59 | 0.69 |
| Fluorosilane | 1.27 | 1.25 | 1.29 | 1.33 | 1.38 | 1.30 | 1.65 | 1.28 | 1.36 | 1.32 | 1.42 | 1.30 | 1.21 | 1.20 |
| s-*cis*-Formic acid | 1.55 | 1.52 | 1.59 | 1.55 | 1.59 | 1.54 | 1.62 | 1.52 | 1.54 | 1.56 | 1.55 | 1.59 | 1.58 | 1.56 |
| s-*trans*-Formic acid | 3.89 | 3.87 | 4.02 | 3.89 | 4.12 | 3.92 | 4.28 | 3.85 | 4.01 | 4.02 | 4.02 | 4.11 | 3.95 | 4.00 |
| GeO | 3.32 | 3.23 | 3.56 | 3.55 | 3.65 | 3.47 | 3.92 | 3.58 | 3.68 | 3.60 | 3.73 | 3.54 | 3.37 | 3.43 |
| $H_2CO$ | 2.33 | 2.31 | 2.41 | 2.34 | 2.57 | 2.35 | 2.72 | 2.26 | 2.43 | 2.40 | 2.44 | 2.51 | 2.27 | 2.41 |
| $H_2O$ | 1.90 | 1.89 | 1.93 | 1.91 | 1.96 | 1.90 | 2.00 | 1.90 | 1.93 | 1.95 | 1.94 | 1.98 | 1.92 | 1.93 |
| $H_2S$ | 1.03 | 1.04 | 1.05 | 1.06 | 1.06 | 1.02 | 1.07 | 0.98 | 1.03 | 1.08 | 1.03 | 1.07 | 0.99 | 1.07 |
| HBr | 0.90 | 0.90 | 0.92 | 0.89 | 0.97 | 0.89 | 0.98 | 0.87 | 0.93 | 0.95 | 0.90 | 0.91 | 0.92 | 0.93 |
| HCCI | 0.14 | 0.09 | 0.01 | 0.10 | 0.08 | 0.11 | 0.17 | 0.15 | 0.04 | 0.04 | 0.13 | 0.02 | 0.09 | 0.09 |
| HCl | 1.14 | 1.14 | 1.16 | 1.16 | 1.15 | 1.13 | 1.12 | 1.12 | 1.14 | 1.15 | 1.15 | 1.16 | 1.15 | 1.18 |
| HCN | 3.02 | 3.00 | 3.07 | 3.02 | 3.13 | 3.02 | 3.13 | 2.99 | 3.06 | 3.03 | 3.06 | 3.12 | 3.02 | 3.03 |
| HF | 1.83 | 1.82 | 1.86 | 1.84 | 1.89 | 1.84 | 1.95 | 1.84 | 1.87 | 1.88 | 1.88 | 1.89 | 1.87 | 1.87 |
| $HfO_2$ | 7.90 | 7.92 | 8.41 | 8.04 | 8.55 | 8.10 | 8.75 | 8.06 | 8.38 | 8.47 | 8.40 | 8.61 | 8.32 | 8.32 |
| HfO | 3.39 | 3.50 | 3.56 | 3.26 | 3.65 | 3.52 | 4.95 | 3.38 | 3.91 | 3.48 | 3.75 | 3.47 | 3.51 | 3.60 |
| HI | 0.44 | 0.44 | 0.48 | 0.40 | 0.56 | 0.43 | 0.65 | 0.37 | 0.49 | 0.52 | 0.41 | 0.47 | 0.48 | 0.38 |
| Imidazole | 3.71 | 3.70 | 3.75 | 3.67 | 3.82 | 3.71 | 3.81 | 3.66 | 3.75 | 3.78 | 3.73 | 3.83 | 3.69 | 3.73 |
| Ketene | 1.48 | 1.46 | 1.48 | 1.46 | 1.55 | 1.47 | 1.67 | 1.42 | 1.49 | 1.51 | 1.51 | 1.53 | 1.45 | 1.49 |
| KF | 8.35 | 8.29 | 8.53 | 8.52 | 8.62 | 8.45 | 8.58 | 8.54 | 8.62 | 8.62 | 8.67 | 8.70 | 8.50 | 8.61 |
| LaO | 3.88 | 3.80 | 3.87 | 3.66 | 3.82 | 4.02 | 4.05 | 4.09 | 3.93 | 3.65 | 3.89 | 3.64 | 4.65 | 4.22 |
| LiOH | 4.41 | 4.35 | 4.43 | 4.39 | 4.48 | 4.37 | 4.42 | 4.46 | 4.45 | 4.39 | 4.46 | 4.49 | 4.39 | 4.52 |
| Methylamine | 1.29 | 1.30 | 1.28 | 1.28 | 1.35 | 1.28 | 1.37 | 1.25 | 1.32 | 1.31 | 1.28 | 1.30 | 1.25 | 1.27 |
| Methylphosphine | 1.18 | 1.21 | 1.21 | 1.19 | 1.20 | 1.16 | 1.15 | 1.06 | 1.13 | 1.17 | 1.14 | 1.23 | 1.10 | 1.22 |
| Methylsilane | 0.80 | 0.77 | 0.81 | 0.78 | 0.77 | 0.80 | 0.50 | 0.72 | 0.70 | 0.82 | 0.69 | 0.92 | 0.71 | 0.86 |
| $N_2O$ | 0.01 | 0.03 | 0.18 | 0.04 | 0.26 | 0.10 | 0.76 | 0.01 | 0.28 | 0.29 | 0.32 | 0.21 | 0.19 | 0.23 |
| NaCl | 8.84 | 8.77 | 8.89 | 8.74 | 8.95 | 8.75 | 8.78 | 8.96 | 8.87 | 8.79 | 8.90 | 9.07 | 8.91 | 9.13 |
| $NH_3$ | 1.54 | 1.54 | 1.55 | 1.56 | 1.57 | 1.53 | 1.55 | 1.53 | 1.56 | 1.56 | 1.53 | 1.55 | 1.54 | 1.53 |
| NiH | 2.52 | 2.59 | 3.00 | 2.75 | 3.06 | 2.66 | 3.70 | 2.49 | 3.01 | 3.41 | 3.16 | 3.58 | 2.83 | 3.02 |
| Nitrobenzene | 4.63 | 4.61 | 4.62 | 4.51 | 4.73 | 4.61 | 4.92 | 4.53 | 4.65 | 4.62 | 4.64 | 4.68 | 4.65 | 4.64 |
| Nitromethane | 3.53 | 3.52 | 3.64 | 3.46 | 3.73 | 3.58 | 3.98 | 3.47 | 3.69 | 3.68 | 3.68 | 3.77 | 3.62 | 3.65 |

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Table 8 (*continued*)

| Molecule | τ-HCTHhyb | TPSSh | MPWB1K | M05 | M05-2X | PW6B95 | M06-HF | M06 | M06-2X | M08-HX | M08-SO | M11 | MN12-SX | MN15 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Nitrosyl hydride | 1.66 | 1.68 | 1.75 | 1.64 | 1.80 | 1.70 | 1.89 | 1.63 | 1.74 | 1.74 | 1.77 | 1.83 | 1.66 | 1.75 |
| $PH_3$ | 0.62 | 0.65 | 0.64 | 0.65 | 0.65 | 0.59 | 0.76 | 0.54 | 0.61 | 0.66 | 0.63 | 0.63 | 0.54 | 0.63 |
| Phenol | 1.27 | 1.26 | 1.29 | 1.28 | 1.32 | 1.27 | 1.38 | 1.27 | 1.30 | 1.31 | 1.29 | 1.32 | 1.29 | 1.29 |
| *cis*-Propyleneimine | 1.79 | 1.77 | 1.78 | 1.75 | 1.87 | 1.78 | 1.93 | 1.73 | 1.80 | 1.79 | 1.78 | 1.85 | 1.69 | 1.78 |
| *trans*-Propyleneimine | 1.61 | 1.61 | 1.62 | 1.58 | 1.70 | 1.61 | 1.73 | 1.58 | 1.64 | 1.63 | 1.62 | 1.68 | 1.55 | 1.63 |
| Propyne | 0.85 | 0.83 | 0.82 | 0.83 | 0.84 | 0.83 | 0.84 | 0.80 | 0.81 | 0.82 | 0.79 | 0.84 | 0.79 | 0.82 |
| RbCl | 10.71 | 10.69 | 10.87 | 10.81 | 10.93 | 10.76 | 10.75 | 10.82 | 10.89 | 10.84 | 10.88 | 11.11 | 10.92 | 10.95 |
| RbF | 8.86 | 8.82 | 9.03 | 9.00 | 9.09 | 8.96 | 8.99 | 9.04 | 9.07 | 9.10 | 9.16 | 9.25 | 9.08 | 9.02 |
| ScF | 2.34 | 2.41 | 2.46 | 2.31 | 2.37 | 2.50 | 3.41 | 2.40 | 2.63 | 2.75 | 2.90 | 1.61 | 2.41 | 2.48 |
| ScO | 3.37 | 3.48 | 3.80 | 3.08 | 4.04 | 3.79 | 4.58 | 4.05 | 4.19 | 3.99 | 4.06 | 3.40 | 3.27 | 3.94 |
| $SeO_2$ | 2.78 | 2.70 | 2.94 | 2.90 | 3.02 | 2.88 | 3.21 | 2.92 | 2.98 | 2.98 | 3.08 | 3.06 | 2.85 | 2.89 |
| $SO_2$ | 1.64 | 1.60 | 1.72 | 1.68 | 1.84 | 1.70 | 1.99 | 1.71 | 1.80 | 1.78 | 1.81 | 1.78 | 1.66 | 1.69 |
| SrO | 8.53 | 8.46 | 9.28 | 8.66 | 9.55 | 8.85 | 10.14 | 8.86 | 9.35 | 9.54 | 9.47 | 9.72 | 9.12 | 9.26 |
| TiH | 2.76 | 2.63 | 2.62 | 3.48 | 2.15 | 2.69 | 1.56 | 3.45 | 2.13 | 2.57 | 2.97 | 2.39 | 3.40 | 3.35 |
| TiN | 4.34 | 4.14 | 3.27 | 3.44 | 3.26 | 3.35 | 3.29 | 3.58 | 3.30 | 3.27 | 3.17 | 2.89 | 7.04 | 3.31 |
| TiO | 3.35 | 3.43 | 3.58 | 3.43 | 3.60 | 3.54 | 4.12 | 3.56 | 3.73 | 3.63 | 3.77 | 3.12 | 3.31 | 3.64 |
| TlBr | 4.62 | 4.64 | 4.67 | 4.93 | 5.08 | 4.68 | 4.87 | 4.75 | 5.24 | 5.48 | 4.90 | 4.95 | 4.65 | 4.68 |
| TlCl | 4.62 | 4.59 | 4.62 | 4.93 | 4.89 | 4.66 | 4.66 | 4.74 | 5.10 | 5.30 | 4.91 | 4.86 | 4.57 | 4.64 |
| TlF | 4.14 | 4.04 | 4.19 | 4.50 | 4.36 | 4.24 | 4.19 | 4.40 | 4.49 | 4.59 | 4.58 | 4.39 | 4.02 | 4.16 |
| TlI | 4.53 | 4.56 | 4.58 | 4.61 | 5.21 | 4.56 | 5.24 | 4.38 | 5.31 | 5.68 | 4.67 | 5.03 | 4.55 | 4.47 |
| VN | 4.05 | 3.13 | 3.01 | 4.47 | 2.86 | 3.09 | 2.70 | 4.43 | 2.91 | 2.89 | 3.97 | 2.77 | 4.28 | 4.22 |
| VO | 3.62 | 3.58 | 3.65 | 3.55 | 3.46 | 3.57 | 3.81 | 3.41 | 3.40 | 3.82 | 4.02 | 3.39 | 5.00 | 3.78 |
| YO | 4.37 | 4.41 | 4.63 | 4.33 | 4.67 | 4.67 | 5.13 | 4.75 | 4.69 | 4.56 | 4.46 | 4.19 | 4.15 | 4.85 |
| $ZrO_2$ | 7.74 | 7.77 | 8.11 | 7.73 | 8.25 | 7.89 | 8.42 | 7.85 | 8.10 | 8.16 | 8.09 | 8.23 | 8.11 | 8.10 |
| ZrO | 2.99 | 3.40 | 3.23 | 2.26 | 3.32 | 3.19 | 4.45 | 2.39 | 3.55 | 3.44 | 3.12 | 3.90 | 2.56 | 2.94 |
| MUE (MR)[a] | 0.41 | 0.32 | 0.44 | 0.40 | 0.56 | 0.35 | 0.96 | 0.40 | 0.51 | 0.56 | 0.66 | 0.55 | 0.81 | 0.48 |
| MUE (SR)[b] | 0.13 | 0.13 | 0.14 | 0.15 | 0.21 | 0.12 | 0.32 | 0.13 | 0.19 | 0.23 | 0.17 | 0.23 | 0.15 | 0.15 |
| MUE (all)[c] | 0.20 | 0.18 | 0.22 | 0.22 | 0.31 | 0.18 | 0.49 | 0.20 | 0.28 | 0.32 | 0.30 | 0.32 | 0.33 | 0.24 |
| MSE (all)[d] | 0.07 | 0.05 | 0.16 | 0.09 | 0.27 | 0.10 | 0.43 | 0.10 | 0.23 | 0.28 | 0.25 | 0.24 | 0.23 | 0.18 |
| General-purpose? | Yes | Yes | Yes | Yes | No | Yes | Yes | Yes | No | No | No | Yes | Yes | Yes |
| | τ-HCTHhyb | TPSSh | MPWB1K | M05 | M05-2X | PW6B95 | M06-HF | M06 | M06-2X | M08-HX | M08-SO | M11 | MN12-SX | MN15 |

[a] Mean unsigned error calculated over 20 multi-reference molecules. [b] Mean unsigned error calculated over 53 single-reference molecules. [c] Mean unsigned error calculated over all the 73 molecules. [d] Mean signed error calculated over all the 73 molecules.

multi-reference systems, which is only slightly better than what was obtained with HLE16 (0.88 D). Of the two meta-NGAs, the overall MUE of the recently developed MN15-L functional (0.24 D) is slightly better than MN12-L (0.27 D). The overall MUE over 73 molecules shows that the best results for this category of exchange–correlation functional are given by TPSS followed by MGGA_MS2 and M06-L. The decreasing MUE for multi-reference systems in proceeding from MN12-L to MN15-L shows encouraging progress on the path toward improvement.

Tables 6 and 7 show dipole moments for 14 hybrid GGAs (BHandHLYP, B3LYP, B1LYP, mPW1PW, B97-1, PBE0, MPW1K, B3LYP*, CAM-B3LYP, MPW3LYP, B97-3, LC-ωPBE, HSE06 and SOGGA11-X), one hybrid NGA (N12-SX), and the popular molecular-mechanics-corrected method, B3LYP-D3(BJ). For single-reference systems we again see that all the 15 functionals do very well and have MUEs less than 0.20 D. On the other hand for multi-reference systems, large errors (MUEs $\geq$ 0.32 D) are obtained. The errors are large especially for functionals that have a high percentage of HF exchange, for example, CAM-B3LYP (19 to 65%), LC-ωPBE (0 to 100%), BHandHLYP (50%), MPW1K (42.8%), and SOGGA11-X (40.15%), and their poor performance is not unexpected given the fact that functionals with high HF exchange are often known to be unreliable for energetics of multi-reference systems. The effect of the percentage of HF exchange can be easily seen with the functionals, B3LYP* and B3LYP that have the same ingredients and differ only in *X*. (These functionals have 15% and 20% HF exchange, respectively). As the percentage of HF exchange increases from B3LYP* to B3LYP, we see that the MUE for the multi-reference set increases from 0.34 to 0.37 D, while their MUEs on single-reference set is around 0.13 D. B1LYP has a different correlation functional than B3LYP, but the same exchange functional, and as *X* is increased further to 25%, the MUE for the multi-reference set increases to 0.41 D. The B97-1 and B97-3 functionals provide another example in that higher HF exchange in B97-3 compared to B97-1 leads to larger MUE for multi-reference systems (0.35 D with B97-3 and 0.32 D with B97-1).

Overall, B97-1, PBE0 and HSE06 functionals are the best performing functionals in Tables 6 and 7. The PBE0 functional has the same percentage of HF exchange as B1LYP, but different exchange and correlation functional forms, and it does better than B1LYP on the multi-reference set. The HSE06 functional has the same functional form as PBE0 except that PBE0 is a global hybrid and has 25% HF exchange at all interelectronic separations whereas HSE06 is a range-separated hybrid and has 25% HF exchange at short interelectronic separations but no HF exchange at long interelectronic separations; these two functionals

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give the same results to the number of decimal places reported in the table, which shows that short-range interelectronic distances have the dominant effect on the dipole moments.

In Table 6, there is negligible difference in dipole moments predicted by B3LYP and B3LYP-D3(BJ) even though the molecules were consistently optimized with both the methods. This can be expected (but we nevertheless added this check at the request of a reviewer) because the molecular-mechanics correction in B3LYP-D3(BJ) is simply added on after the SCF calculation with B3LYP and so does not change the density. Thus the only change in the dipole moment is due to the change in optimized geometry, but the changes in geometry for the molecules in this study are very small because none of the molecules tested in this study are van der Waals complexes (which are the only cases for which the molecular mechanics correction should make a significant change in geometry).

Table 8 shows results obtained using 12 hybrid meta-GGA and two hybrid meta-NGA functionals that involve kinetic energy density as well as HF exchange. Again most of the functionals do well for single-reference systems with MUE $< 0.20$ D. The M06-HF functional, which has the biggest MUE (0.49 D) in the table is of a special type in having 100% HF exchange at all interelectronic separations. It performs poorly for multi-reference systems, which is again expected given its very high percentage of HF exchange. In contrast, TPSSh with only 10% HF exchange does reasonably well for multi-reference systems, and in this category of functionals, the TPSSh functional (along with PW6B95) gives the best performance over all the 73 molecules, mainly because of its good performance on multi-reference systems due to the small percentage of HF exchange. The rest of the functionals have percentages of HF exchange between those of TPSSh and M06-HF, and also have MUEs for multi-reference systems that are in between the MUEs for these two functionals. The functionals that have HF exchange in the range 15–30% (τ-HCTHhyb, PW6B95, M05 and M06) yield MUEs in the range 0.30–0.41 D, the ones that have values around 50% or more yield larger errors.

The poor performance of functionals with high HF exchange for multi-reference systems has been attributed to the fact that HF exchange brings in static correlation error.[3] However, the slightly worse general performance for dipole moments as HF exchange is raised is less a cause for concern, since raising the percentage of Hartree–Fock exchange often gives a considerable improvement in main-group bond energies, barrier heights, and excitation energies, so a very slight decrease in accuracy of dipole moments is acceptable. We also caution the reader that one should not base decisions on very small differences in the MUEs for dipole moments since small differences could be caused by methodological issues such as that we compare dipole moments calculated at equilibrium geometries to experimental ones that are averaged over zero point and thermal vibration motions.

## 5. Conclusions

The dipole moments of a variety of neutral organic and inorganic molecules were examined using 48 density functionals with various combinations of ingredients. Of the 73 molecules included in our calculation of mean unsigned errors, 53 were found by using $B_1$ diagnostics to be single-reference molecules, and all the 48 methods tested here were found to give good performance for these 53 single-reference molecules. For the remaining 20 multi-reference molecules, functionals with high HF exchange or high local exchange were found to give large errors. In particular, HLE16 and HLE17 that have high local exchange and M06-HF that has 100% HF exchange were found to give large mean unsigned errors, where for the latter case it is consistent with previous recommendations not to use such functionals for multi-reference systems. For the entire set of 73 molecules, the hybrid GGAs B97-1 and PBE0, the range-separated hybrid GGA HSE06, and the hybrid meta-GGAs TPSSh and PW6B95 were found to the best performing functionals each with an MUE of 0.18 D. All these functionals were also found to be the best performing functionals for multi-reference systems.

Probably the most interesting result, though, and also a very encouraging result, is the finding that – despite the great diversity in the density functionals tested – the quality of their predictions for dipole moments are very similar, at least for single-reference molecules. If we do not consider the seven functionals that were not designed as general-purpose functionals, the functional with 100% Hartree–Fock exchange for all interelectronic distances, and the molecular-mechanics-corrected functional, there remains 39 diverse functionals, and their average MUE is 0.23 D, with a standard deviation of only 0.04 D. If we consider only single-reference molecules, the MUE averaged over 47 functionals (excluding only the molecular-mechanics-corrected one, so we have an even more diverse set of functionals than the 39 considered for the whole set of data) is 0.16 D, again with a standard deviation of only 0.04 D.

We conclude there is not a lot of difference in the ability of various density functionals to represent the first moment of the electron density. Furthermore, all density functionals tested so far are considerably better for charge distributions of single-reference molecules than for charge distributions of multi-reference molecules.

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