Density Functionals for Inorganometallic and Organometallic Chemistry

Nathan E. Schultz, Yan Zhao, and Donald G. Truhlar*

Department of Chemistry and Supercomputing Institute, University of Minnesota, 207 Pleasant Street Southeast, Minneapolis, Minnesota 55455-0431

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We present a database of 21 bond dissociation energies for breaking metal−ligand bonds. The molecules in the metal−ligand bond energy database are AgH, CoH, CoO^+, $CoOH^+$, $CrCH_3^+$, $CuOH_2^+$, FeH, $Fe(CO)_5$, FeO, FeS, LiCl, LiO, MgO, $MnCH_3^+$, $NiCH_2^+$, $Ni(CO)_4$, RhC, VCO^+, VO, and VS. We have also created databases of metal−ligand bond lengths and atomic ionization potentials. The molecules used for bond lengths are AgH, BeO, CoH, CoO^+, FeH, FeO, FeS, LiCl, LiO, MgO, RhC, VO, and VS and the ionization potentials are for the following atoms: C, Co, Cr, Cu, Ni, O, and V. The data were chosen based on their diversity and expected reliability, and they are used along with three previously developed databases (transition metal dimer bond energies and bond lengths and main-group molecular atomization energies) for assessing the accuracy of several kinds of density functionals. In particular, we report tests for 42 previously defined functionals: 2 local spin density approximation (LSDA) functionals, 14 generalized gradient approximation (GGA) methods, 13 hybrid GGA methods, 7 meta GGA methods, and 8 hybrid meta GGA methods. In addition to these functionals, we also examine the effectiveness of scaling the correlation energy by testing 13 functionals with scaled or no gradient-corrected correlation energy, and we find that functionals of this kind are more accurate for metal−metal and metal−ligand bonds than any of the functionals already in the literature. We also present a readjusted GGA and a hybrid GGA with parameters adjusted for metals. When we consider these 57 functionals for metal−ligand and metal−metal bond energies simultaneously with main-group atomization energies, atomic ionization potentials, and bond lengths we find that the most accurate functional is G96LYP, followed closely by MPWLYP1M (new in this article), XLYP, BLYP, and MOHLYP (also new in this article). Four of these five functionals have no Hartree−Fock exchange, and the other has only 5%. As a byproduct of this work we introduce a convenient diagnostic, called the B_1 diagnostic, for ascertaining the multireference character in a bond.

1. Introduction

Density functional theory[1] (DFT) has become the preferred method for calculating a variety of molecular properties, such as thermochemistry and thermochemical kinetics. Hybrid DFT, in which the functional contains a small amount of Hartree−Fock exchange, has been shown to be superior to nonhybrid DFT for both atomization energies[2] and barrier heights[3,4] of main group elements. However, we have recently shown that nonhybrid DFT functionals are significantly more accurate than hybrid DFT methods for the atomization energies of transition metal dimers.[5] Therefore, we expect that metal−ligand binding, especially transition metal−ligand binding energies, since they involve both transition metals and main group elements, will pose a difficult challenge to DFT.

Some research groups have already benchmarked the accuracy of DFT methods for metal−ligand systems. Although the number of DFT functionals studied in each study is small (5 or less), the general conclusion is that hybrid methods are favored as the most accurate way to treat the energetics of transition metal−ligand complexes.[6−8] A recent review by Harrison confirms this finding;[7] in particular he reviews the electronic structure of transition metal−main group diatomics and states that the hybrid B3LYP functional is the most promising functional for transition metal diatomics. B3LYP, however, has been found to be less accurate than more recent methods for main group thermochemistry[4] and significantly less accurate than its nonhybrid counterpart, BLYP, for metal−metal bonding.[5] It therefore seems unlikely that B3LYP would be the most accurate functional for metal−ligand bonding.

In the present study, we have assembled a large and diverse data set, and we use it for testing existing density functionals and developing new ones. We have included several systems that have been used in previous computational studies, such as MCH_2^+ and MCH_3^+,[8−10] MH,[8,11] MCO,[12] and MO[13,14] complexes, where M is a metal atom. In addition to these systems, aqua ions, as pointed out in the recent paper by Rotzinger,[15] are of great interest and have a different character from organometallic complexes; hence we have included a system of the MH_2O^+ type in our database. We have also included a number of metal−ligand systems where the metal atom is not a transition element, but rather a main-group element. Systems of this type are known to be challenging for theoretical methods,[14] and we include one MCl system and three MO systems in which M is a main-group metal. Putting the whole, diverse set of test cases together, we have a database of 21 experimental metal−ligand binding energies (also called bond dissociation energies, henceforth just called bond energies or BEs) that we use to test 42 DFT functionals from the literature as well as some new methods that are presented for the first time in this paper. In addition to bond energies, we have constructed a small database of atomic ionization potentials that we also use to test the DFT methods. The ionization potentials that we include are C, Co, Cr, Cu, Ni, O, and V.

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In general, bonds between metal atoms, sometimes called metallic bonds, are best thought of as a special type of covalent bond in which one cannot transform the zero-order reference wave function to a localized description,[16] at least not without an appreciable increase in energy because of the lack of a significant gap in the electronic band structure, that is the presence of nearly degenerate electronic configurations. In current popular terminology the lack of a significant gap is labeled as a mulireference[17] situation. Multireference situations are found not only in metals but also (to varying degrees) in nonmetallic bond-breaking processes and in many transition states and open-shell molecules. A question we will ask in this article is how to classify molecules involving metal atoms so as to best identify the types of systems that are treated with different degrees of success (or failure) by DFT. Should we treat transition metals as different from main-group metals? Should we organize systems into those with metal−metal bonds and those with only metal−nonmetal bonds, independent of their degree of multireference character? Or should we organize systems by their degree of multireference character, independent of their connectivity?

2. Databases

The full database that we have developed and that we present here is called MLBE21/05 (metal−ligand bond energies of 21 compounds assembled in 2005), and it contains the zero-point-energy-exclusive BEs (also called equilibrium BEs) of AgH, BeO, CoH, CoO^+, $CoOH^+$, $CrCH_3^+$, $CuOH_2^+$, FeH, $Fe(CO)_5$, FeO, FeS, LiCl, LiO, MgO, $MnCH_3^+$, $NiCH_2^+$, $Ni(CO)_4$, RhC, VCO^+, VO, and VS. The metal−ligand bond energies (BE) are defined as the zero-point-exclusive energy for either process

$$ML_n \rightarrow M + nL \tag{1}$$

or

$$ML_n^+ \rightarrow M^+ + nL \tag{2}$$

In eqs 1 and 2, M is a transition metal atom, L is a ligand, and n is the number of ligands.

The CoH, CoO^+, $CoOH^+$, $CrCH_3^+$, $CuOH_2^+$, FeH, $MnCH_3^+$, $NiCH_2^+$, and VCO^+ data come from Armentrout,[18] the $Fe(CO)_5$ datum comes from Schultz et al.,[19] the FeS, VO, and VS data come from Bridgeman et al.,[20] the $Ni(CO)_4$ data come from Sunderlin et al.,[21] and the datum for RhC comes from DaBell et al.[22] The FeO bond energy is computed as an average of the values quoted by Armentrout (101.3 ± 3.6 kcal/mol) et al.[18] and Merer (96.1 ±1.8 kcal/mol).[23] The only nonexperimental data is the bond energy of AgH, which comes from the high-level ab initio calculation of Li et al.[24]

We note that the experimental uncertainity for $CuOH_2^+$, 1.9 kcal/mol, is larger than the uncertainty for most of our data; however, this system is included because metal ion−water systems are very important, and the value reported by Armentrout, 38.8 kcal/mol when adjusted for zero-point effects, agrees quite well with the complete-basis-set limit of CCSD(T), namely the value of 38.5 kcal/mol reported by Feller et al.[25] The main group-ligand BEs (LiO, LiCl, BeO, and MgO) come from Database/4,[26] which is available via the Internet (http://comp.chem.umn.edu/database/).

The experimental bond energies (sometimes called ground-state BEs or D_0) correspond to 0 K, and hence they include zero-point energy, whereas MLBE21/05 contains zero-point-energy-exclusive values. The literature values for BeO, LiCl, LiO, and MgO had already been adjusted for zero-point energy effects. The remaining 17 complexes were adjusted in this work for zero-point effects by computing the zero-point energies associated with the bond dissociation process, namely the zero-point energies for the transition metal−ligand complex, denoted $E_{ZPE}(ML_n)$, and the ligand, denoted $E_{ZPE}(L)$. The experimental equilibrium BEs are then computed as $BE = D_0 + \Delta E_{ZPE}$, where

$$\Delta E_{ZPE} = f(E_{ZPE}(ML_n) - nE_{ZPE}(L)) \tag{3}$$

and $E_{ZPE}(ML_n)$ and $E_{ZPE}(L)$ are calculated with B3LYP, and f is a scale factor that was determined in an earlier paper.[5] Note that, in the above formula, the $E_{ZPE}(ML_n)$ is to be replaced with $E_{ZPE}(ML_n^+)$ in the case of a cationic complex. In these ZPE calculations, the compact effective core potential method of Stevens et al.[27−29] was used for the transition elements, and the 6-31G(2d,p) basis set was used for the main group elements. The accuracy of the scaled ZPEs is better than 0.1 kcal/mol (see the Supporting Information). The DZQ basis set and the B3LYP functional are described in more detail in the next section.

We also consider a database of bond lengths, consisting of equilibrium internuclear distances for AgH, BeO, CoH, CoO^+, FeH, FeO, FeS, LiCl, LiO, MgO, RhC, VO, and VS. We call this database MLBL13/05 (metal−ligand bond lengths of 13 compounds). The database contains values of r_e and not r_0, where r_e is the bond length at equilibrium, and r_0 is the bond length in the ground vibrational state. The r_e values for AgH, BeO, LiCl, and MgO were taken from Huber and Herzberg,[30] and those for CoH, FeH, FeO, LiO, RhC, and VO were taken from Ram et al.,[31] Phillips et al.,[32] Taylor et al.,[33] Yamada et al.,[34] DaBell et al.,[22] and Lagerqvist and Selin,[35] respectively. The r_e values for CoO^+, FeS, and VS were obtained from the experimental r_0 values by a method that is described in the Supplementary Information.

In addition to the two new metal−ligand databases, MLBE21/05 and MLBL13/05, we will also present comparison to the transition-metal atomization energy database, TMAE9/05, which is fully described in our previous paper,[5] and the AE6 database[36] of atomization energies for main-group molecules. The dissociation products in MLBE21/05 and TMAE9/05 include both the neutral and cationic charge states of five metal atoms (Co, Cr, Cu, Ni, and V), and we used these to start a database of 7 ionization potentials (IPs), called IP7/05, which contains the five metal IPs and the IPs for C and O. In addition to the IP7/05 database, we also use a database called IP3 (Cr, Cu, and O) for the purposes of optimizing functionals. The IP data come from Moore's reference books.[37]

The experimental data for the three new databases are summarized in Table 1.

3. Computational Methods

All of the calculations in this paper have been carried out with Gaussian03 or a modified version of Gaussian 03.[38] We will test previously developed functionals from five different categories of DFT methods: LSDA, GGA, hybrid GGA, meta GGA, and hybrid meta GGA methods. The LSDA functionals depend only on the electron density. The GGA functionals depend explicitly on the gradient of the electron density as well as the density itself; hybrid GGA functionals depend on Hartree−Fock (HF) exchange as well as the electron density and its gradient. Meta GGA functionals depend on the electron density, its gradient, and the kinetic energy density. The hybrid meta GGA functionals depend on HF exchange, the electron density and its gradient, and the kinetic energy density. We will

TABLE 1: Data (kcal/mol and Å) Used for IP7/05, MLBE21/05 and MLBL13/05

		BE	r_e		IP
AgH	$^1\Sigma^+$	54.0	1.618	C	256.7
BeO	$^1\Sigma$	104.8	1.331	Co	181.7
CoH	$^3\Phi$	45.6	1.531	Cr	156.0
CoO^+	$^5\Delta$	76.1	1.646	Cu	178.2
$CoOH^+$	$^4A''$	73.8		Ni	176.2
$CrCH_3^+$	$^5A_1$	28.8		O	314.0
CuH_2O^+	$^1A_1$	38.8		V	155.6
FeH	$^4\Delta$	36.9	1.610		
$Fe(CO)_5$	$^1A_1$	147.4			
FeO	$^5\Delta$	102.6	1.616		
FeS	$^5\Delta$	76.7	2.013		
LiCl	$^1\Sigma$	113.9	2.021		
LiO	$^2\Pi$	82.0	1.689		
$MnCH_3^+$	$^6A_1$	51.9			
MgO	$^1\Sigma$	59.2	1.749		
$NiCH_2^+$	$^2A_1$	76.3			
$Ni(CO)_4$	$^1A_1$	144.7			
RhC	$^2\Sigma^+$	139.2	1.613		
VCO^+	$^5\Delta$	28.2			
VO	$^4\Sigma^-$	149.9	1.589		
VS	$^4\Sigma^-$	106.9	2.048		

speak of LSDA, GGA, hybrid GGA, meta GGA, and hybrid meta GGA when specifically referring to one of the subsets, whereas the phrase "DFT functionals" remains general and does not exclude hybrid, LSDA, or meta functionals. The phrase "hybrid functionals" will refer to both hybrid GGA and hybrid meta GGA functionals, and "nonhybrid functionals" will refer to LSDA, GGA, and meta GGA functionals.

In addition to the GGA functionals described above, we will test two kinds of less conventional approaches. The first unconventional approach, which was proposed by Hertwig and Koch,[39] is called GGE (generalized gradient exchange). GGE functionals consist of GGA exchange functionals and LSDA correlation functionals. The second kind of unconventional functional that we consider is called GGSC (generalized gradient with scaled correlation), and this kind of functional is new in this article. In the GGSC functionals, the Kohn−Sham operator can be written as

$$F = F^{\mathrm{SE}} + F^{\mathrm{GCE}} + F^{\mathrm{LC}} + (Y/100)F^{\mathrm{GCC}} \qquad (4)$$

where F^{SE} is the Slater local density functional,[40] F^{GCE} is the gradient correction to the LSDA exchange, F^{LC} is the LSDA correlation functional, and F^{GCC} is the gradient correction to the LSDA correlation. The GGE functionals may be considered a special case of the GGSC ones in which Y is set equal to 0, but in the present article we will set $Y = 50$ for two functionals.

The LSDAs that we assess in the present article are SWVN3[40,41] and SPWL.[40,42] It should be noted that the PWL (Perdew−Wang local) correlation functional used is not the same functional as the 1981 local correlation functional that is referred to as Perdew−Zunger.[43] However, VWN3, PWL, and Perdew−Zunger all represent fits to the same data of Ceperley and Alder.[44] The GGA functionals that we will test are (in alphabetical order) BLYP,[45,46] BP86,[45,47] BPBE,[45,48] BPW91,[45,49] G96LYP,[46,50] HCTH[51] (also called HCTH407), mPWLYP,[46,52] mPWPBE,[48,52] mPWPW91,[52] OLYP,[46,53] PBE (PBE exchange with PBE correlation, also called PBEPBE),[48] and XLYP.[46,54] The hybrid GGA functionals that we are using are B3LYP,[45,46,55] B3P86,[45,47] B3PW91,[2,45,49] B97-1,[51] B97-2,[56] B98,[57] BH&HLYP,[38,45,46] MPW1K,[49,52,58] mPW1PW91 (also called mPW0 and MPW25),[49,52] MPW3LYP,[4,46,52] O3LYP,[46,53,59] PBE1PBE (also called PBE0),[48,60,61] and X3LYP.[46,54] The meta DFT functionals that we test here are BB95,[45,62] mPWB95,[52] PBEKCIS,[48,63] TPSS (TPSS exchange with TPSS correlation, also called TPSSTPSS),[64] TPSSKCIS (TPSS exchange with KCIS correlation),[63,64] mPWKCIS,[52,63,65] and VSXC.[66] The hybrid meta GGA functionals that we study in this paper are B1B95,[45,62] BB1K,[45,62,65] MPW1B95,[52,62,65] MPWB1K,[52,62,65] MPW1KCIS,[52,63,65] PBE1KCIS,[48,63,67] TPSS1KCIS,[49,63−65] and TPSSh (uses TPSS exchange and TPSS correlation).[68,69] The GGE functionals that we test are BPWL, BVWN5, G96VWN5, G96PWL, mPWPWL, mPWVWN5, OPWL, OVWN5, TPSSPWL, and TPSSVWN5. The GGSC methods that we optimize and test are called G96HLYP and MOHLYP, where the HLYP acronym indicates that we use 50% of the LYP correlation functional (or half-LYP) and MO stands for metal-optimized OptX. The method is described in more detail in Section 10.

Several hybrid methods (B3LYP, B3P86, B3PW91, MPW3LYP, and X3LYP) also involve a Y-parameter that is not unity; however, we continue to place these methods in the hybrid GGA category because, in general, the errors are much more sensitive to the percentage X of Hartree−Fock exchange than to Y. This taxonomy may be somewhat cumbersome, but we have found that the single most important facet of a DFT method is whether HF exchange is incorporated into the functional, and our classification of functionals reflects this. GGE and GGSC functionals are described in more detail in section 5.5. The compositions of the functionals tested here are summarized in Table 2, where they are listed in alphabetical order for the reader's convenience. Table 2 also gives X, which is the percentage of Hartree−Fock exchange, and Y, which is the percentage of gradient-corrected correlation.

We will also test two levels of basis set in this paper; these levels are denoted DZQ and TZQ, which stand for double-ζ quality and triple-ζ quality, respectively. The DZQ and TZQ basis sets for the transition elements were defined in our previous paper,[5] and we extend them to include main group elements in this article. For the main group elements, the 6-31+G(d,p)[70] and MG3[71,72] basis sets are used in DZQ and TZQ basis sets, respectively. In both this article and ref 5, all calculations on transition-metal atoms and on molecules containing one or more transition metals use 5D, 7F spherical harmonic basis functions for d and f shells on all atoms. Otherwise, for example, for DZQ calculations on LiCl, we use the standard option, which is 6D Cartesian functions for 6-31+G(d,p).

4. Spin−Orbit Correction

The DFT calculations do not include spin−orbit coupling, and to compare to experiment this must be included. For the general process $ML_n \rightarrow M + nL$ we must consider three possible spin−orbit energies, namely those for ML_n, M, and L. The bond energies in this paper are computed by the formula

$$\mathrm{BE} = \mathrm{BE(DFT)} + \Delta E_{\mathrm{SO}} \qquad (5)$$

where

$$\Delta E_{\mathrm{SO}} \equiv nE_{\mathrm{SO}}(\mathrm{L}) + E_{\mathrm{SO}}(\mathrm{M}) - E_{\mathrm{SO}}(\mathrm{ML}_n) \qquad (6)$$

and all values on the right-hand side of eq 6 are negative numbers because the spin−orbit effect lowers the energy of the ground state. Note that M and ML_n in eq 6 are replaced by M^+ and ML_n^+, respectively, for cationic metal−ligand complexes. For the IP database, the general process that we must consider is $X \rightarrow X^+$, where X is an atomic system. The spin−orbit correction used in the IP calculations is $\Delta E_{\mathrm{SO}} \equiv E_{\mathrm{SO}}(X^+) -$

TABLE 2: Summary of the DFT Methods Used in This Paper[a]

	X	*Y*	type	exchange functional[b]/correlation functional[b]
B1B95	28	100	HMGGA	Beck88/Perdew86/Becke95
B3LYP	20	81	HGGA	Beck88/Perdew86/Lee−Yang−Parr
B3P86	20	81	HGGA	Beck88/Perdew86/
B3PW91	20	81	HGGA	Beck88/Perdew86/Perdew-Wang91
B97-1	21	100	HGGA	B97-1/B97-1
B97-2	21	100	HGGA	B97-2/B97-2
B98	21.98	100	HGGA	B98/B98
BB1K	42	100	HMGGA	Beck88/Perdew86/Becke95
BB95	0	100	MDFT	Beck88/Perdew86/Becke95
BH&HLYP	50	100	HGGA	Beck88/Perdew86/Lee−Yang−Parr
BLYP	0	100	GGA	Beck88/Perdew86/Lee−Yang−Parr
BP86	0	100	GGA	Beck88/Perdew86/Perdew86
BPBE	0	100	GGA	Beck88/Perdew86/Perdew−Burke−Ernzerhof
BPW91	0	100	GGA	Beck88/Perdew86/Perdew−Wang91
BPWL	0	0	GGE	Beck88/Perdew86/Perdew−Wang local
BVWN5	0	0	GGE	Beck88/Perdew86/VWN no. 5
G96LYP	0	100	GGA	Gill96/Lee−Yang−Parr
G96HLYP	0	50	GGSC	Gill96/half-Lee−Yang−Parr
G96PWL	0	0	GGE	Gill96/Perdew−Wang local
G96VWN5	0	0	GGE	Gill96/VWN no. 5
HCTH	0	100	GGA	Hamprecht−Cohen−Tozer−Handy/Hamprecht−Cohen−Tozer−Handy
mPW1B95	31	100	HMGGA	modified Perdew−Wang91/Becke95
MPW1K	42.8	100	HGGA	modified Perdew−Wang91/Perdew−Wang91
mPW1PW91[c]	25	100	HGGA	modified Perdew−Wang91/Perdew−Wang91
MPW3LYP	21.8	87.1	HGGA	modified Perdew−Wang91/Lee−Yang−Parr
mPWB95	0	100	MDFT	modified Perdew-Wang91/Becke95
MPW1KCIS	15	100	HMGGA	modified Perdew−Wang91/Krieger−Chen−Iafrate−Savin
mPWKCIS	0	100	MDFT	modified Perdew−Wang91/Krieger−Chen−Iafrate−Savin
MPWKCIS1K	41	100	HMGGA	modified Perdew−Wang91/Krieger−Chen−Iafrate−Savin
MOHLYP	0	50	GGSC	metal-adjusted OptX/half-Lee−Yang−Parr
mPWLYP	0	100	GGA	modified Perdew−Wang91/Lee−Yang−Parr
MPWLYP1M	5	100	HGGA	MPW with 1 par. for metals/Lee−Yang−Parr
mPWPBE	0	100	GGA	modified Perdew−Wang91/Perdew−Burke−Ernzerhof
mPWPW91	0	100	GGA	modified Perdew−Wang91/Perdew−Wang91
mPWPWL	0	0	GGE	modified Perdew−Wang91/Perdew−Wang local
mPWVWN5	0	0	GGE	modified Perdew−Wang91/VWN no. 5
O3LYP	11.61	78	HGGA	OptX/Lee−Yang−Parr
OLYP	0	100	GGA	OptX/Lee−Yang−Parr
OPWL	0	0	GGE	OptX/Perdew−Wang local
OVWN5	0	0	GGE	OptX/VWN no. 5
PBE	0	100	GGA	Perdew−Burke−Ernzerhof/Perdew−Burke−Ernzerhof
PBE1KCIS	22	100	HMGGA	Perdew−Burke−Ernzerhof/Krieger−Chen−Iafrate−Savin
PBE1PBE[d]	25	100	HGGA	Perdew−Burke−Ernzerhof/Perdew−Burke−Ernzerhof
PBEKCIS	0	100	MGGA	Perdew−Burke−Ernzerhof/Krieger−Chen−Iafrate−Savin
PBEPWL	0	0	GGE	Perdew−Burke−Ernzerhof/Perdew−Wang local
PBEVWN5	0	0	GGE	Perdew−Burke−Ernzerhof/VWN no. 5
SVWN3	0	0	LSDA	Slater/VWN no. 3
SPWL	0	0	LSDA	Slater/Perdew−Wang local
TPSS	0	100	MDFT	Tao−Perdew−Staroverov−Scuseria/Tao−Perdew−Staroverov−Scuseria
TPSS1KCIS	13	100	HMGGA	Tao−Perdew−Staroverov−Scuseria/Krieger−Chen−Iafrate−Savin
TPSSh	10	100	HMGGA	Tao−Perdew−Staroverov−Scuseria/Tao−Perdew−Staroverov−Scuseria
TPSSKCIS	0	100	MDFT	Tao−Perdew−Staroverov−Scuseria/Krieger−Chen−Iafrate−Savin
TPSSPWL	0	0	GGE	Tao-Perdew-Staroverov-Scuseria/Perdew-Wang local
TPSSVWN5	0	0	GGE	Tao-Perdew-Staroverov-Scuseria/VWN no. 5
VSXC	0	100	MDFT	van Voorhis−Scuseria/van Voorhis−Scuseria
X3LYP	21.8	87.1	HGGA	Becke88 + Perdew-Wang91/Lee−Yang−Parr
XLYP	0	100	GGA	Becke88 + Perdew-Wang91/Lee−Yang−Parr

[a] GGA stands for generalized-gradient approximation, GGE stands for generalized-gradient exchange, GGSC stands for generalized-gradient exchange with scaled correlation, HGGA stands for hybrid GGA, HMGGA stands for hybrid meta GGA, MGGA stands for meta GGA, and LSDA stands for local spin density approximation. [b] In each case the exchange functional is listed first and the correlation functional is listed second. [c] Also called mPW0 and MPW25. [d] Also called PBE0.

$E_{\mathrm{SO}}(\mathrm{X}^+)$. The values of ΔE_{SO} used in the BE and IP calculations are given in Table 3.

The spin−orbit effects for the atoms and atomic ions were calculated from the atomic spectral information listed in Moore's reference books.[37] The spin−orbit effects for the metal−ligand complexes were estimated by calculating the first-order splitting of a multiplet, which can be calculated by using equation (V,8) in Herzberg's book.[73] This only estimates the splitting of a multiplet term and does not account for second-order spin−orbit splitting.[74] For several of the metal−ligand complexes there is no first-order spin−orbit splitting because they are either closed-shell singlets or have Σ or A ground states. The metal−ligand complexes that have nonzero spin−orbit splitting are CoH, CoO^+, FeH, FeO, FeS, LiO, and VCO^+. The spin−orbit coupling constants for CoH,[75] FeH,[76] FeO,[23] FeS,[77] and LiO[34] are known experimentally, and thus we can easily calculate the spin−orbit splitting. There is no spin−orbit coupling constant available for CoO^+ and VCO^+. We have calculated the spin−orbit energy of CoO^+ by scaling the spin−orbit energy of the isoelectronic FeO by 1.16; the factor of 1.16 was used because

TABLE 3: Experimental Spin−Orbit Energies (ΔE_{SO}) in kcal/mol

		MLBE21/05[a]		IP7/05[b]
AgH	$^1\Sigma^+$	0.00	C	−0.04
BeO	$^1\Sigma^+$	−0.02	Co	0.27
CoH	$^3\Phi$	−0.37	Cr	0.00
CoO^+	$^5\Delta$	−0.76	Cu	0.00
$CoOH^+$	$^4A''$	−2.19	Ni	1.06
$CrCH_3^+$	$^5A1$	0.00	O	0.02
CuH_2O^+	$^1A1$	0.00	V	0.33
FeH	$^4\Delta$	−0.12		
$Fe(CO)_5$	$^1A1$	−1.52		
FeO	$^5\Delta$	−0.09		
FeS	$^5\Delta$	−1.20		
LiCl	$^1\Sigma^+$	−0.84		
LiO	$^2\Pi$	0.14		
MgO	$^1\Sigma$	−0.02		
$MnCH_3^+$	$^6A1$	0.00		
$NiCH_2^+$	$^2A1$	−1.72		
$Ni(CO)_4$	$^1A1$	−2.78		
RhC	$^2\Sigma^+$	−4.34		
VCO^+	$^5\Delta$	0.00		
VO	$^4\Sigma^-$	−0.94		
VS	$^4\Sigma^-$	−1.47		

[a] $\Delta E_{SO} \equiv nE_{SO}(L) + E_{SO}(M) - E_{SO}(ML_n)$, where n is the number of ligands, $E_{SO}(L)$ is the spin−orbit energy of the ligand, $E_{SO}(M)$ is the spin−orbit energy of the metal atom/ion, and $E_{SO}(ML_n)$ is the spin−orbit energy of the metal−ligand complex. [b] $\Delta E_{SO} \equiv E_{SO}(X^+) - E_{SO}(X)$, where $E_{SO}(X^+)$ is the spin−orbit energy of the cation and $E_{SO}(X)$ is the spin−orbit energy of the neutral atom.

the spin−orbit energy scales as Z^4, where Z is nuclear charge. Due to the nature of the VCO^+ bond, the open shell molecular orbitals of VCO^+ will be similar to the open shell atomic orbitals of V^+; therefore, we approximate the spin−orbit energy of VCO^+ with the spin−orbit energy of V^+. Although the ground states calculated by DFT methods tend to not always agree with experiment or WFT, we nevertheless use the accurate spin−orbit energy in eq 6 so that tests presented here are always equivalent to comparing experimental energies that have the experimental spin−orbit effect removed to DFT calculations without spin−orbit effects. The spin−orbit energies for the ligands were taken from Fast et al.[78]

5. Bond Energies and Atomization Energies

5.1. Atomic and Molecular Ground States. The experimental BEs correspond to dissociation of the metal−ligand complex in its ground electronic state to the ground electronic states of the metal atom (or ion) and ligands. As was pointed out in our paper on transition metal dimers,[5] different DFT methods will often predict different ground electronic states for a molecule or atom. Therefore, the calculated BE for each combination of DFT functional and basis set combination is not calculated by forcing the ground states of the atoms, ions, ligands, or metal−ligand complexes to have ground electronic states that agree with either experimental results or ab initio wave function calculations. In other words we always calculate BE using the ground state for the atoms and metal−ligand complexes as predicted by each DFT functional and basis set combination. We do not wish to dwell on this issue in this paper, but will briefly discuss some of the issues in this section.

The atomic ground states may be either $Ns^2(N-1)d^n$ or $Ns^1(N-1)d^{n+1}$, where N is the highest principal quantum number of the atom and n is the number of d-electrons in shell $N-1$. However, DFT methods will often favor the $Ns^1(N-1)d^{n+1}$ state or a mixture of the $Ns^1(N-1)d^{n+1}$ and $Ns^2(N-1)d^n$ states for all atoms even if ab initio wave function theory and experimental results predict a $Ns^2(N-1)d^n$ state. In this paper, we generate multiple guesses for each atom to ensure that we have found the lowest energy state for each DFT method/basis set combination.

For most of the metal−ligand complexes, the ground states predicted by each combination of DFT functional and basis set combination agree well with all of the other DFT calculations in this paper and ab initio wave function theory and experimental results. For some metal−ligand complexes, though, in particular CoH, CoO^+, $CoOH^+$, FeH, FeS, and VCO^+, there is no agreement among the DFT methods as to which electronic state is the lowest energy state.

The two hydrides will be discussed first. Bauschlicher and Langhoff[79] have calculated the spectroscopic constants of the transition metal hydride diatomics in great detail, and they predict the ground states of CoH and FeH to be $^3\Phi$ and $^4\Delta$, respectively. Their results agree well with experimental results[75,80] and with several other calculations that have been reviewed by Harrison.[7] In our studies, all of the DFT methods predict that the electronic ground state of CoH is $^3\Phi$ with the DZQ basis set, but roughly half of the DFT methods predict that the electronic ground state of CoH is $^3\Delta$ and the other half predict a $^3\Phi$ ground state with the TZQ basis set. For FeH, all of the DFT methods predict a $^4\Delta$ ground electronic state when the DZQ basis set is used; when the TZQ basis set is used, about half of the DFT methods predict a $^4\Delta$ ground electronic state state and the other half predict a $^4\Phi$ electronic state.

We turn now to FeS. It has been found by DFT studies[20] and experimental studies[77,81] that the ground electronic state of FeS is a $^5\Delta$ state. However, it has been proposed by Hübner et al.[82] using ab initio wave functions that the ground electronic state of FeS is a $^5\Sigma$ state. In our studies, nearly all of the DFT methods with both basis sets (DZQ and TZQ) predict a $^5\Delta$ ground state for FeS. The only exceptions to this are the SPWL and VSXC methods with the DZQ basis set, which predict that FeS has a $^5\Sigma$ ground electronic state.

There have been relatively few computational studies on VCO^+ and no experimental predictions as to the ground electronic state of VCO^+. The computational studies by Barnes et al.[83] and Gutsev et al.[84] predict that the ground state of VCO^+ is a $^5\Delta$ state. We find that all of the methods predict a $^5\Delta$ ground state, except for some of the hybrid GGA methods with the TZQ basis set, which predict a $^5\Sigma$ ground state.

A study of $CoOH^+$ by Ricca and Bauschlicher[85] indicates that the lowest-energy state of $CoOH^+$ is a quartet, but they do not assign a ground-state symmetry. A later theoretical study[86] yielded $^4A'$ for the ground electronic state symmetry. In our studies, when the TZQ basis set is used, nearly all of the nonhybrid methods predict a $^4A'$ ground state and nearly all of hybrid methods predict a $^4A''$ state. Most of the DFT functionals predict a $^4A''$ state when the DZQ basis set is used.

5.2. Bond Energies. The errors for the bond energies are given in Table 4. The table gives the mean signed errors (MSEs) and mean unsigned errors (MUEs), as well as the average of the MUEs (AMUEs) with the two basis sets. The error is taken as the difference between theory and experiment, so a negative MSE indicates that the methods under bind and a positive MSE indicates that the methods over bind. The AMUE denotes the average mean unsigned error and is the average of the MUEs with the DZQ and TZQ basis levels. We compute the AMUE because it is useful to have a DFT method that does not need to be used with a specific basis set, and we would like our conclusions to be valid not only for small molecules but also for larger systems where the system sizes preclude the use of

TABLE 4: The Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Average Mean Unsigned Error (AMUE) for the MLBE21/05 Database of Bond Energies[a]

	DZQ		TZQ		
method	MSE	MUE	MSE	MUE	AMUE[b]
		LSDA			
SPWL	28.2	28.2	29.6	29.6	28.9
SVWN3	30.2	30.2	31.7	31.7	30.9
		GGA			
BLYP	7.1	8.0	9.0	9.6	8.8
BP86	10.1	10.7	11.8	12.2	11.4
BPBE	6.6	7.6	8.4	9.1	8.3
BPW91	6.6	7.5	8.4	9.0	8.3
G96LYP	5.3	6.9	7.0	7.7	7.3
HCTH	4.9	5.7	7.3	7.6	6.6
mPWLYP	8.8	9.4	10.9	11.3	10.4
mPWPBE	8.4	9.1	10.2	10.7	9.9
mPWPW91	8.4	9.1	10.2	10.6	9.8
OLYP	2.6	5.0	4.9	6.3	5.7
PBE	9.7	10.4	11.7	12.1	11.3
XLYP	7.9	8.6	10.1	10.6	9.6
		hybrid GGA			
B3LYP	−2.7	6.9	−0.6	6.0	6.5
B3P86	0.9	5.7	2.6	6.0	5.8
B3PW91	−3.0	6.4	−1.3	5.8	6.1
B97-1	−2.5	7.4	0.6	5.4	6.4
B97-2	−2.2	6.1	−0.2	5.2	5.7
B98	−3.5	7.9	−0.4	5.8	6.8
BH&HLYP	−19.0	19.3	−17.1	17.6	18.5
MPW1K	−14.1	15.1	−12.3	13.6	14.4
mPW1PW91	−5.4	8.3	−3.7	6.8	7.6
MPW3LYP	−2.4	7.5	−0.5	6.1	6.8
O3LYP	−1.6	5.6	0.3	5.3	5.5
PBE1PBE	−4.4	7.6	−2.7	6.3	6.9
X3LYP	−3.2	7.3	−1.1	5.9	6.6
		meta GGA			
BB95	10.9	11.5	12.6	12.9	12.2
mPWB95	12.7	13.2	14.5	14.6	13.9
mPWKCIS	7.5	8.3	11.3	11.8	10.0
PBEKCIS	9.0	9.6	11.8	12.2	10.9
TPSS	5.5	7.1	7.4	7.9	7.5
TPSSKCIS	6.3	7.2	8.5	9.0	8.1
VSXC	6.3	7.0	6.3	6.6	6.8
		hybrid meta GGA			
B1B95	−3.8	7.0	−3.0	6.4	6.7
BB1K	−12.5	13.3	−10.2	11.2	12.3
MPW1B95	−5.8	8.3	−3.3	6.7	7.5
MPW1KCIS	−0.9	5.6	0.8	5.5	5.6
MPWKCIS1K	−13.8	16.0	−12.8	14.0	15.0
PBE1KCIS	−3.7	7.4	−2.1	6.2	6.8
TPSSh	0.3	5.8	2.1	5.5	5.7
TPSS1KCIS	−0.3	5.5	1.2	5.3	5.4

[a] All values in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

TABLE 5: The Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Average Mean Unsigned Error (AMUE) Averaged over MLBE21/05 and TMAE9/05 Databases of Bond Energies, Weighted Equally[a]

	DZQ		TZQ		
method	MSE	MUE	MSE	MUE	AMUE[b]
		LSDA			
SPWL	24.9	24.9	28.8	28.8	26.9
SVWN3	27.6	27.6	32.2	32.2	29.9
GGA					
BLYP	2.7	5.7	6.9	7.4	6.6
BP86	4.8	8.9	8.7	9.9	9.4
BPBE	−0.5	8.1	2.8	7.6	7.8
BPW91	−0.9	8.3	2.7	7.6	7.9
G96LYP	−0.5	6.6	3.6	6.3	6.4
HCTH	5.9	7.2	9.3	9.8	8.5
mPWLYP	4.9	6.5	9.3	9.5	8.0
mPWPBE	1.9	8.4	5.4	8.6	8.5
mPWPW91	1.6	8.6	5.3	8.5	8.6
OLYP	−2.3	6.8	1.1	7.0	6.9
PBE	4.5	9.1	7.8	9.9	9.5
XLYP	3.6	6.1	8.2	8.5	7.3
		hybrid GGA			
B3LYP	−11.6	13.8	−8.6	11.4	12.6
B3P86	−8.8	12.0	−6.1	10.4	11.2
B3PW91	−13.7	15.4	−11.2	13.4	14.4
B97-1	−10.6	14.0	−3.1	7.0	10.5
B97-2	−7.1	9.8	−1.9	5.3	7.6
B98	−11.3	14.0	−4.7	7.8	10.9
BH&HLYP	−28.3	28.5	−25.7	26.0	27.2
MPW1K	−24.0	24.5	−22.0	22.6	23.6
mPW1PW91	−15.8	17.2	−14.5	16.0	16.6
MPW3LYP	−11.5	14.0	−8.3	11.1	12.6
O3LYP	−9.2	11.2	−6.2	9.3	10.3
PBE1PBE	−14.5	16.1	−11.0	15.7	15.9
X3LYP	−11.9	13.9	−9.2	11.6	12.8
		meta GGA			
BB95	9.0	12.0	11.1	11.2	11.6
mPWB95	11.3	13.1	13.7	13.8	13.4
mPWKCIS	1.7	7.4	6.4	8.9	8.2
PBEKCIS	3.9	7.9	8.4	9.7	8.8
TPSS	−0.3	7.8	3.1	7.0	7.4
TPSSKCIS	0.3	7.2	3.9	7.4	7.3
VSXC	5.3	9.2	5.9	8.4	8.8
		hybrid meta GGA			
B1B95	−13.8	15.4	−12.5	14.1	14.8
BB1K	−21.2	21.6	−18.9	19.4	20.5
MPW1B95	−14.3	15.6	−12.0	13.7	14.6
MPW1KCIS	−9.9	12.3	−7.3	10.5	11.4
MPWKCIS1K	−23.8	24.9	−22.1	22.7	23.8
PBE1KCIS	−13.5	15.4	−11.2	13.3	14.3
TPSSh	−7.5	10.6	−4.4	8.3	9.5
TPSS1KCIS	−9.2	11.8	−5.4	8.6	10.2

[a] All values in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

large basis sets. Some workers prefer to use root-mean-square errors (RMSEs) rather than MUEs. Therefore, to complement the data in the printed tables, there is a table in the Supporting Information that gives RMSEs. By presenting only MSEs and MUEs rather than all three types of errors in the printed version of this article, we hope to make it more readable. The reported errors in all cases are per metal−ligand bond, so the errors for $Ni(CO)_4$ and $Fe(CO)_5$ are divided by 4 and 5, respectively, before the MSEs, MUEs, RMSEs, or AMUEs are computed.

The difference between hybrid and nonhybrid methods is smaller for metal−ligand systems than for transition metal dimers. The hybrid GGA methods, on average, have an MUE of 8.5 and 7.4 kcal/mol with the DZQ and TZQ basis sets, respectively. The GGA methods, on the other hand, have MUEs of 8.2 and 9.7 kcal/mol with the DZQ and TZQ basis sets, respectively. Focusing only on MUEs, the most accurate methods with the DZQ and TZQ basis sets are OLYP and B97-2, respectively, where the MUEs for OLYP/DZQ and B97-2/TZQ are 5.0 and 5.2 kcal/mol, respectively. The method that has the lowest AMUE is TPSS1KCIS, which has an AMUE of 5.4 kcal/mol. It should be noted that several methods have AMUEs that are almost as good as TPSS1KCIS, namely, OLYP, B3P86, B97-2, O3LYP, MPW1KCIS, and TPSSh, which all have AMUEs less than 6.0 kcal/mol.

To put our results into a broader context, Table 5 presents the MSE, MUE, and AMUE averaged over both the MLBE21/05 and TMAE9/05 databases, with equal weighting for the databases, even though one has more molecules. In this broader test, G96LYP has the lowest AMUE, in particular 6.4 kcal/mol, and TPSS1KCIS has the 20th lowest

AMUE 10.2 kcal/mol. Focusing only on the MUE with the TZQ basis set, B97-2 has the lowest MUE (5.3 kcal/mol). B97-2, as noted earlier, is somewhat of an anomaly for hybrid methods, in that the MUEs and AMUEs of B97-2 are more similar to the nonhybrid methods than they are to the hybrid methods for these metal systems. However, B97-2 has also been shown to be among the most accurate methods for nonmetal systems.[4] The B97-2 functional is again recommended for general-purpose usage, and we will discuss some of our attempts to develop a new general-purpose metal functional in Section 10.

5.3. Effects of Static Correlation. It is now widely recognized[2,87−93] that the exchange functionals include some static correlation (also called near-degeneracy correlation, internal correlation, and left-right correlation) and they also include some dynamical correlation[94] (which is the instantaneous correlation of electronic motions primarily at short interelectronic distances), whereas the correlation functionals include only dynamical correlation. (However, it has been pointed out that although DFT functionals include some static correlation, they do so in an incomplete way.[93]) For most closed-shell main-group molecules at or near their equilibrium geometry, one may obtain a good zero-order wave function without considering static correlation. However, static correlation becomes important when one has near-degeneracy effects. Open-shell molecules containing one or more metal atom often have important static correlation effects on their bond energies and even their equilibrium structures. In such cases, it appears that replacing some percentage of the DFT exchange, which includes static correlation, by Hartree−Fock exchange, which does not, significantly degrades the quality of the theoretical model.[5] Even in open-shell molecules not containing metal atoms, DFT is known to incorporate near-degeneracy effects significantly better than Hartree−Fock.[95]

Although these facts are widely appreciated in theory, and there is growing appreciation that nonhybrid functionals are often the most suitable ones for metal−metal bonds,[96−98] it has not been clear what effect static correlation has on numerical calculations of quantities such as metal−ligand bond energies. For example, in the Introduction we mentioned a review[7] that, despite the inadequacy of Hartree−Fock exchange, recommends the hybrid B3LYP function (which has 20% Hartree−Fock exchange) for transition metal diatomics. A symposium volume on catalysis[99] provides a typical overview of current practice; in application articles employing DFT for organometallic, metallic, or metal oxide catalysis, seven employed the hybrid B3LYP functional, and nine employed nonhybrid functionals (four employed BP86, four employed PW91, and one employed BLYP). However, many studies on such systems employ nonhybrid methods for reasons related to cost and computer codes, rather than expected performance. It would be useful to have a better understanding of when hybrid methods are to be preferred and when not. In general, for reasons explained above, we believe that hybrid methods are less useful when there is significant multireference character. There is a general diagnostic for multireference character, called the T_1 diagnostic,[100] but it requires a coupled cluster calculation with quasiperturbative fourth order and fifth order triple excitations, and this is impractical[101] for most interesting applications where DFT is used. In this section, we will propose a less expensive diagnostic for multireference character.

TABLE 6: B_1 Values in kcal/mol[a]

MLBE21/05		TMAE9/05	
AgH	3.4	Ag_2	4.4
BeO	14.2	AgCu	5.5
CoH	3.4	Cu_2	6.7
CoO^+	30.6	Cr_2	54.3
$CoOH^+$	14.3	Mo_2	42.8
$CrCH_3^+$	9.5	Ni_2	39.0
CuH_2O^+	0.5	V_2	68.7
FeH	6.5	ZrV	39.8
$Fe(CO)_5$	12.6	Zr_2	24.0
FeO	30.2		
FeS	18.7		
LiCl	0.8		
LiO	5.9		
MgO	18.9		
$MnCH_3^+$	10.7		
$NiCH_2^+$	22.4		
$Ni(CO)_4$	10.1		
RhC	27.8		
VCO^+	7.1		
VO	26.6		
VS	17.4		

[a] B_1 is the B1LYP diagnostic

We have found in previous work that transition metal dimers are severely under bound when hybrid methods are used if the dimers have significant multireference character.[5] In that paper, we did not propose a diagnostic that could be used to assign which dimers have large multireference character, but instead we based our analysis on MP2 binding energies and multireference ab initio calculations. Out of the 9 dimers studied in that paper (Ag_2, Cr_2, Cu_2, AgCu, Mo_2, Ni_2, V_2, and Zr_2, and ZrV) we made a single-reference subset of atomization energies that contained Ag_2, Cr_2, Cu_2, and Zr_2, where Zr_2 was a borderline case. The errors of the single-reference subset were lower than the errors of the full set for all of the functionals tested, but the single-reference subset errors were significantly lower than the errors for the full database for the hybrid functionals. We now explain this by looking at the effect that static correlation plays on the bond dissociation process. In Table 6 we compute a quantity called the B1LYP-diagnostic (abbreviated B_1), which is defined as

$$B_1 = (\mathrm{BE}_{\mathrm{BLYP}} - \mathrm{BE}_{\mathrm{B1LYP//BLYP}})/n \tag{7}$$

where $\mathrm{BE}_{\mathrm{BLYP}}$ and $\mathrm{BE}_{\mathrm{B1LYP//BLYP}}$ are the BEs computed with BLYP and B1LYP//BLYP,[102] respectively, at the geometry optimized by BLYP, and n is the number of bonds being broken. (For this purpose, “a double bond” counts as one bond, not two.) Note that TMAE9/05 contains dimer atomization energies, which, because they are diatomics, are equivalent to bond energies with $n = 1$. For B1LYP, the percentage of Hartree−Fock exchange is 25%.[102] The B_1 diagnostic is a key quantity because it can be used to isolate the effects of static correlation on the bond dissociation energies. The B_1 diagnostic is a measure of multireference character because the Hartree−Fock exchange approximation fails badly for multireference systems, whereas GGAs can usually handle these systems almost as well as they handle single-reference systems. There is also a connection between the T_1 diagnostic[100] and the B_1 diagnostic in that they both provide a measure of multireference character. However, the B_1 diagnostic is much less expensive to compute. An encouraging sign of consistency between the T_1 and B_1 diagnostic is that published[14] T_1 diagnostic values for BeO and MgO are large, and we find these molecules also have large B_1 diagnostics.

The B_1 values for the MLBE21/05 and TMAE9/05 databases are given in Table 6. First of all we note that main-group metallic compounds, just like compounds containing transi-

TABLE 7: The Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Average Mean Unsigned Error (AMUE) for the Complexes that Have B_1 Values Less Than and Greater than 10 kcal/mol for TMAE9/05[a]

	B_1 < 10 kcal/mol					B_1 > 10 kcal/mol				
	DZQ		TZQ			DZQ		TZQ		
method	MSE	MUE	MSE	MUE	AMUE	MSE	MUE	MSE	MUE	AMUE[b]
					LSDA					
SPWL	15.6	15.6	14.1	14.1	14.8	24.7	24.7	35.0	35.0	29.9
SVWN3	16.6	16.6	15.1	15.1	15.8	29.1	29.1	41.5	41.5	35.3
					GGA					
BLYP	1.9	1.9	−0.4	0.9	1.4	−3.5	4.1	7.4	7.5	5.8
BP86	3.1	3.1	1.2	1.2	2.2	−2.2	9.1	7.8	10.9	10.0
BPBE	0.3	1.1	−1.4	1.4	1.3	−11.7	12.3	−3.7	8.6	10.4
BPW91	0.3	1.1	−1.5	1.5	1.3	−12.6	13.0	−3.6	8.4	10.7
G96LYP	−1.2	1.2	−3.2	3.2	2.2	−8.9	8.9	1.9	5.6	7.3
HCTH	1.4	2.8	−0.8	1.1	1.9	9.6	11.7	17.4	17.4	14.5
mPWLYP	3.7	3.7	1.3	1.3	2.5	−0.2	3.5	10.9	10.9	7.2
mPWPBE	2.2	2.2	0.3	0.7	1.5	−8.0	10.4	0.6	9.4	9.9
mPWPW91	2.2	2.2	0.2	0.7	1.5	−8.7	11.1	0.7	9.3	10.2
OLYP	−5.1	5.1	−6.9	6.9	6.0	−8.1	10.3	−0.7	8.1	9.2
PBE	3.6	3.6	2.0	2.0	2.8	−2.9	9.9	4.9	10.6	10.3
XLYP	0.1	2.7	0.4	0.7	1.7	−0.9	4.1	9.4	9.4	6.8
					hybrid GGA					
B3LYP	−2.6	2.6	−4.2	4.2	3.4	−29.6	29.6	−22.9	22.9	26.3
B3P86	−1.4	1.4	−2.7	2.7	2.1	−26.8	26.8	−20.9	21.0	23.9
B3PW91	−4.1	4.1	−5.4	5.4	4.7	−34.4	34.4	−28.9	28.9	31.7
B97-1	3.0	3.0	2.5	2.5	2.8	−29.5	29.5	−11.5	11.5	20.5
B97-2	2.0	2.0	2.1	2.1	2.1	−18.9	19.3	−6.5	6.9	13.1
B98	1.8	1.8	1.2	1.2	1.5	−29.4	29.4	−14.0	14.0	21.7
BH&HLYP	−9.2	9.2	−10.1	10.1	9.6	−51.9	51.9	−46.5	46.5	49.2
MPW1K	−8.6	8.6	−9.4	9.4	9.0	−46.6	46.6	−42.7	42.7	44.7
mPW1PW91	−4.6	4.6	−5.8	5.8	5.2	−37.0	37.0	−35.0	35.0	36.0
MPW3LYP	−1.5	1.5	−3.2	3.2	2.4	−30.1	30.1	−22.4	22.4	26.3
O3LYP	−6.5	6.5	−7.9	7.9	7.2	−21.9	21.9	−15.2	16.1	19.0
PBE1PBE	−3.5	3.5	−4.5	4.5	4.0	−35.1	35.1	−26.7	35.3	35.2
X3LYP	−4.1	4.1	−3.8	3.8	4.0	−28.9	28.9	−24.1	24.1	26.5
					meta GGA					
BB95	3.9	3.9	2.4	2.4	3.2	8.6	16.7	13.1	13.1	14.9
mPWB95	5.7	5.7	4.1	4.1	4.9	12.0	16.7	17.4	17.4	17.1
mPWKCIS	1.1	1.2	−1.0	1.1	1.2	−6.7	9.3	2.7	8.5	8.9
PBEKCIS	2.5	2.5	1.1	1.1	1.8	−2.9	7.9	7.0	10.3	9.1
TPSS	2.3	2.3	1.1	1.1	1.7	−10.3	11.6	−2.5	8.7	10.2
TPSSKCIS	0.8	0.8	−0.6	1.0	0.9	−8.8	10.3	−0.7	8.3	9.3
VSXC	13.2	13.2	12.3	12.3	12.7	−0.1	10.5	2.1	9.1	9.8
					hybrid meta GGA					
B1B95	−3.1	3.1	−3.8	3.8	3.5	−34.1	34.1	−30.9	30.9	32.5
BB1K	−5.8	5.8	−6.4	6.4	6.1	−41.9	41.9	−38.3	38.3	40.1
MPW1B95	−2.4	2.4	−3.2	3.2	2.8	−33.0	33.0	−29.4	29.4	31.2
MPW1KCIS	−3.1	3.1	−4.8	4.8	3.9	−27.0	27.0	−20.8	20.8	23.9
MPWKCIS1K	−9.2	9.2	−9.7	9.7	9.4	−46.3	46.3	−42.4	42.4	44.3
PBE1KCIS	−3.8	3.8	−4.5	4.5	4.1	−33.1	33.1	−28.2	28.2	30.6
TPSSh	−0.5	0.9	−1.4	1.4	1.1	−22.7	22.7	−15.8	15.8	19.3
TPSS1KCIS	−2.7	2.7	−3.7	3.7	3.2	−25.9	25.9	−16.2	16.2	21.0

[a] All values in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

tion metals, can have very large B_1 diagnostics; examples are BeO and MgO. On the basis of our experience with these systems, we have placed the division between multireference and single-reference molecules at 10 kcal/mol. We realize that this distinction is semiquantitative in that molecules that have values slightly above or below 10 kcal/mol could be placed in either category. The 10 kcal/mol B_1 criterion is consistent for TMAE9/05 with our previous paper[5] if we assign Zr_2 as being a multireference dimer and not (as previously) a single-reference dimer; this classification is not unreasonable because we have previously said[5] that Zr_2 was a borderline case. For MLBE21/05, the single-reference complexes are AgH, CoH, $CrCH_3^+$, CuH_2O^+, FeH, LiCl, LiO, and VCO^+.

Tables 7 and 8 give the mean errors in bond energies when the molecules are sorted into subgroups with B_1 < 10 kcal/mol and B_1 > 10 kcal/mol. Considering TMAE9/05 first (Table 7), we find that there is a stark difference between the single-reference and multireference dimers. The magnitude of the MSEs and the MUEs for the hybrid methods are considerably larger than the nonhybrid errors for the multireference dimers, whereas the hybrid methods perform much better for the single-reference dimers. In fact, the hybrid TPSSh functional is the most accurate method for the single-reference subset. Turning now to MLBE21/05 (Table 8), we do not see a particularly large difference in the MUEs for the hybrid functionals between the single- and multireference subsets except for the three functionals (BH&HLYP, MPW1K, and MPWKCIS1K) that have $X > 30$. Amazingly, though, these three functionals have the lowest AMUEs for B_1 < 10 kcal/mol. It is interesting to note, in contrast to the typical behavior of the unsigned errors, that the signed errors for MLBE21/05 depend strongly on the B_1 diagnostic. The MSEs for the nonhybrid method are posi-

TABLE 8: The Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Average Mean Unsigned Error (AMUE) for the Complexes That Have B_1 Values Less Than and Greater Than 10 kcal/mol in MLBE21/05[a]

	$B_1 < 10$ kcal/mol					$B_1 > 10$ kcal/mol				
	DZQ		TZQ			DZQ		TZQ		
method	MSE	MUE	MSE	MUE	AMUE	MSE	MUE	MSE	MUE	AMUE[b]
					LSDA					
SPWL	20.2	20.2	17.8	17.8	19.0	33.2	33.2	35.3	35.3	34.2
SVWN3	21.0	21.0	19.0	19.0	20.0	35.9	35.9	37.9	37.9	36.9
					GGA					
BLYP	8.0	10.1	7.5	8.9	9.5	6.5	6.6	9.5	9.5	8.1
BP86	9.5	11.1	8.5	9.4	10.2	10.4	10.4	13.1	13.1	11.8
BPBE	5.7	8.0	5.1	6.8	7.4	7.2	7.3	9.9	9.9	8.6
BPW91	5.8	8.1	5.2	6.9	7.5	7.1	7.2	9.7	9.7	8.4
G96LYP	6.1	8.7	5.6	7.5	8.1	4.8	5.8	7.4	7.4	6.6
HCTH	6.2	7.5	6.2	7.0	7.2	4.0	4.6	7.3	7.3	5.9
mPWLYP	9.3	11.1	9.1	10.1	10.6	8.4	8.4	11.4	11.4	9.9
mPWPBE	7.1	9.1	6.3	7.5	8.3	9.2	9.2	11.9	11.9	10.6
mPWPW91	7.2	9.2	6.5	7.6	8.4	9.0	9.0	11.7	11.7	10.4
OLYP	3.8	7.8	4.1	6.9	7.3	1.8	3.2	5.2	5.8	4.5
PBE	7.7	9.6	7.2	8.2	8.9	11.0	11.0	13.7	13.7	12.4
XLYP	8.6	10.6	7.7	9.0	9.8	7.4	7.4	11.0	11.0	9.2
					hybrid GGA					
B3LYP	4.2	6.1	5.3	6.5	6.3	−6.9	7.7	−4.3	5.6	6.5
B3P86	6.6	7.8	6.5	7.0	7.4	−2.7	4.4	−0.1	5.1	4.7
B3PW91	2.9	5.9	3.1	4.9	5.4	−6.7	6.7	−4.2	6.2	6.5
B97-1	4.6	6.1	5.3	6.1	6.1	−6.8	8.3	−2.5	4.8	6.6
B97-2	3.4	5.4	4.3	5.5	5.4	−5.6	6.5	−3.0	5.0	5.8
B98	4.3	5.9	5.0	5.8	5.8	−8.3	9.1	−3.9	5.7	7.4
BH&HLYP	−2.7	3.6	−1.5	2.9	3.2	−29.0	29.0	−26.3	26.3	27.6
MPW1K	−1.9	4.5	−0.6	4.0	4.2	−21.6	21.6	−19.4	19.4	20.5
mPW1PW91	1.9	5.6	2.2	4.5	5.1	−9.9	9.9	−7.5	8.2	9.1
MPW3LYP	5.3	7.1	5.6	6.6	6.9	−7.1	7.7	−4.5	5.7	6.7
O3LYP	3.0	6.8	3.6	6.4	6.6	−3.7	4.8	−1.1	4.1	4.4
PBE1PBE	2.3	5.9	2.5	4.7	5.3	−8.6	8.6	−6.1	7.1	7.8
X3LYP	4.0	5.9	4.6	6.1	6.0	−7.7	8.1	−4.7	5.7	6.9
					meta GGA					
BB95	8.0	9.6	7.8	8.4	9.0	12.7	12.7	15.0	15.0	13.9
mPWB95	9.2	10.5	8.9	9.2	9.8	14.8	14.8	17.2	17.2	16.0
mPWKCIS	7.6	9.4	12.3	13.5	11.4	7.5	7.5	10.1	10.1	8.8
PBEKCIS	8.5	10.2	10.5	11.4	10.8	9.3	9.3	12.0	12.0	10.6
TPSSTPSS	6.9	8.8	7.6	8.7	8.8	4.3	5.6	6.9	7.1	6.3
TPSSKCIS	7.5	9.4	7.3	8.2	8.8	5.9	6.3	8.4	8.4	7.3
VSXC	8.2	9.9	6.8	7.6	8.8	5.0	5.2	5.7	5.7	5.4
					hybrid meta GGA					
B1B95	2.5	5.5	2.9	4.9	5.2	−7.6	8.0	−6.6	7.3	7.6
BB1K	−3.0	5.2	−0.3	3.0	4.1	−18.2	18.2	−15.9	15.9	17.1
MPW1B95	0.6	6.0	3.5	5.0	5.5	−9.8	9.8	−7.5	7.8	8.8
MPW1KCIS	4.4	6.6	4.5	6.0	6.3	−4.1	5.0	−1.6	5.0	5.0
MPWKCIS1K	0.6	5.2	−0.3	3.6	4.4	−22.6	22.6	−20.1	20.1	21.3
PBE1KCIS	3.6	6.1	3.7	5.3	5.7	−8.2	8.2	−5.8	6.7	7.5
TPSSh	5.4	7.9	5.8	6.9	7.4	−2.8	4.6	−0.5	4.3	4.5
TPSS1KCIS	4.7	7.3	4.7	6.1	6.7	−3.3	4.4	−1.2	4.4	4.4

[a] All values in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

tive for $B_1 < 10$ kcal/mol and remain positive when $B_1 > 10$ kcal/mol, whereas the MSEs for the hybrid methods (with a few exceptions) are all positive for $B_1 < 10$ kcal/mol and then are uniformly negative for $B_1 > 10$ kcal/mol.

The magnitudes of the mean errors in Table 7 are very consistent with what we would expect upon sorting the cases according to their B_1 values, namely, errors are smaller for small B_1 values, and introducing Hartree−Fock exchange makes the results much worse for molecules with large B_1. However, the situation is more complicated in Table 8. A good illustration of this is provided by comparing the results in Table 8 for nonhybrid BP86 to those for hybrid B3P86. When $B_1 < 10$ kcal/mol, B3P86 is favored, as would be expected. However, when $B_1 > 10$ kcal/mol, B3P86 performs better than BP86. Apparently the results involve some cancellation of errors.

We conclude, on the basis of Tables 7 and 8, as well as detailed examination of the results for individual molecules, that it is more advantageous to keep metal−metal bond energies separate from metal−ligand ones for the purpose of analyzing trends than to separate small-B_1 and large-B_1 cases. It is better to have representative data sets for transition-metal dimers and metal−ligand systems than to mix these systems into data sets for small and large B_1, although a division of the data in four sets, as in Tables 7 and 8, provides the best representation.

5.4. Represenative Data Sets. The creation of new data sets is very important in testing and validating computational methods; however, diverse data sets are often quite large and prohibit testing a large number of computational methods against them. Earlier work[36] has demonstrated that it is possible to begin with a large data set and then considerably reduce its size by selecting the most representative pieces of data that can reproduce the errors of the larger database.

Following the previous prescription[36] for building representative data sets, we find a subset that minimizes the root-mean-square deviation (RMSD) between the three standard errors (MSE, MUE, and RMSE) calculated using MLBE21/05 and the same errors using a small subset, e.g., the deviation between the MSE using MLBE21/05 (MSE(ML21)) and the MSE using a small subset (MSE(SS)). The RMSD is calculated with eq 8, where we sum the errors of all 84 methods considered so far (42 DFT functionals, each with two basis sets)

$$\mathrm{RMSD} = \left[\frac{1}{252}\sum_{i=1}^{84}[[(\mathrm{MSE}_i(\mathrm{ML21}) - \mathrm{MSE}_i(\mathrm{SS}))]^2 + [\mathrm{MUE}_i(\mathrm{ML21}) - \mathrm{MUE}_i(\mathrm{SS}))]^2 + [(\mathrm{RMSE}_i(\mathrm{ML21}) - \mathrm{RMSE}_i(\mathrm{SS}))]^2\right]^{1/2} \quad (8)$$

The mean error (ME) is defined as

$$\mathrm{ME} = \left[\frac{1}{252}\sum_{i=1}^{84}(|\mathrm{MSE}_i(\mathrm{ML21})| + \mathrm{MUE}_i(\mathrm{ML21}) + \mathrm{RMSE}_i(\mathrm{ML21}))\right] \quad (9)$$

and the percentage error in representation is defined as

$$\mathrm{PEIR} = 100\% \times \frac{\mathrm{RMSD}}{\mathrm{ME}}. \quad (10)$$

We have examined all sets of n molecules ($n = 2-7$) and found the lowest possible RMSD for each set of n.

The PEIRs for $n = 2-7$ are 20%, 17%, 14%, 13%, 13%, and 11%, respectively. These values correspond to RMSDs of 1.9, 1.6, 1.3, 1.2, 1.2, and 1.0 kcal/mol, respectively. We elect, based on the best compromise of accuracy and cost, to choose the subset of data with $n = 4$ to be our representative subset of metal−ligand data. This subset of data, called MLBE4/05, contains the bond energies of $\mathrm{CrCH_3}^+$, $\mathrm{Fe(CO)_5}$, $\mathrm{NiCH_2}^+$, and VS. The errors for all 57 functionals considered in this article, with both basis sets for MLBE4/05, are given in the Supporting Information. We recommend the use of the MLBE4/05 database for further testing and development when time does not permit use of the full database. The MLBE4/05 database is also a useful complement to TMAE4/05[5] and AE6,[36] which are represenative databases of 4 transition metal bond energies and 6 nonmetal atomization energies, respectively.

5.5. GGE and GGSC Methods. It has been well documented that the atomization energies of nonmetal systems, and some main-group metal systems, are largely overestimated if one uses nonhybrid functionals, whereas this systematic over binding can be largely corrected by incorporating Hartee−Fock exchange into the density functional. In fact, there is a large literature, following Becke,[2] that theoretically justifies the use of HF exchange, but this literature is based almost entirely on main-group chemistry, although there is also some purely theoretical work justifying ∼25% Hartree−Fock exchange.[103,104] However, present results, as well as some previous work, show that bonds involving metal atoms may be exceptions to those arguments. BLYP was recommended in a previous paper[5] for transition metal bonding, and it has an MSE and MUE of 4.8 and 5.3 kcal/mol, respectively, against the TMAE9/05 database with the TZQ basis set. Interestingly, B3LYP has an MSE and MUE of −16.7 and 16.7 kcal/mol, respectively, against the TMAE9/05 database with the same basis set; clearly the hybrid functional is unsatisfactory, which is consistent with the theoretical discussion in Section 5.3. This trend is similar for other pairs of methods such as mPWPW91 and its hybrid counterpart, mPW1PW91. On the basis of the poor performance of Hartree−Fock exchange for transition metal bonding, it would be advantageous to have a method that can cancel the large over binding in DFT without having to incorporate Hartree−Fock orbital exchange. Additional reasons to search for better nonhybrid functionals are that they can be used in codes that cannot handle hybrid functionals and that they can be used for situations such as bulk metals and plane-wave basis sets, where Hartree−Fock exchange causes problems. Furthermore, it is easier to develop efficient algorithms for large systems with nonhybrid functionals than with hybrid ones.

With these motivations in mind, we tested a series of functionals that use a gradient-corrected exchange functional and only a local correlation functional. As explained in Section 3, these functionals are called GGE functionals. The local correlation energy functionals that we include in the test are VWN5[41] and PWL,[42] and the exchange functionals that we test in conjunction with these are Becke88 (further abbreviated B), Gill96 (further abbreviated G96), mPW, OptX (further abbreviated O), PBE, and TPSS. We also consider functionals, called GGSC functionals, where the gradient-corrected correlation is scaled rather than eliminated. We have optimized Y, which is defined by eq 4, for the following correlation functionals: LYP,[46] PBE,[48] and PW91.[49] We note that PBE and PW91 reduce to the PWL[42] functional when $Y = 0$. We also note that LYP is a total correlation functional and is not a gradient correction to an LSDA functional. For the case of LYP, the gradient-corrected correlation energy can be scaled by defining the correlation functional, F^{C}, as

$$F^C = \left(1 - \frac{Y}{100}\right)F^{\mathrm{LC}} + \left(\frac{Y}{100}\right)F^{\mathrm{LYP}} \quad (11)$$

where F^{LC} and F^{LYP} are the local correlation functional and LYP correlation functional, respectively; we use the VWN5[41] local correlation functional for F^{LC}.

The MSEs, MUEs, and AMUEs against MLBE21/05, TMAE9/05, and averaged over the MLBE21/05 and TMAE9/05 databases for the GGE functionals and one GGSC functional are given in Table 9. (Note that we will discuss the GGSC functional, G96HLYP, in the next paragraph.) Comparison of the first section of Table 9 to Table 4 shows that the GGE results obtained with $Y = 0$ are as accurate for MLBE21/05 as the most accurate of the 42 previously defined methods. We especially note that the two best GGE methods, OPWL and OVWN5, for MLBE21/05 have errors that differ by a few tenths of a kcal/mol from TPSS1KCIS and thus can be considered equally as accurate. Unfortunately, the second section of Table 9 shows that OPWL and OVWN5 have the largest errors of any of the GGE methods for TMAE9/05. However, the PBEPWL and PBEVWN5 methods are more accurate than any of the 42 previously defined methods when tested against TMAE9/05. Since the improvement is only a few tenths of a kcal/mol, it might be more appropriate to say that PBEPWL or PBEVWN5 functionals with $Y = 0$ can provide results that are equivalent to standard GGA methods with $Y = 100$. The GGE functionals are among the most accurate methods when the errors are averaged over both databases, as in the last section of Table 9, which can be compared to Table 5. In fact,

TABLE 9: The Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Average Mean Unsigned Error (AMUE) Averaged over the MLBE21/05 and TMAE9/05 Databases of Bond Energies[a]

	DZQ		TZQ		
method	MSE	MUE	MSE	MUE	AMUE[b]
		MLBE21/05			
BPWL	2.9	6.0	4.4	6.7	6.4
BVWN5	2.8	6.0	4.8	7.2	6.6
G96PWL	0.6	5.6	2.3	6.0	5.8
G96VWN5	0.6	5.6	2.2	6.0	5.8
mPWPWL	4.6	6.7	6.2	7.4	7.1
mPWVWN5	4.5	6.7	6.1	7.4	7.0
OPWL	−1.4	5.9	0.5	5.5	5.7
OVWN5	−1.5	6.0	0.5	5.4	5.7
PBEPWL	5.7	7.1	7.7	8.3	7.7
PBEVWN5	5.7	7.1	7.5	8.2	7.7
TPSSPWL	3.4	6.2	2.8	5.9	6.1
TPSSVWN5	3.5	6.1	2.9	5.7	5.9
G96HLYP	3.2	5.7	4.8	6.5	6.1
		TMAE9/05			
BPWL	−9.3	9.3	−3.1	4.6	6.9
BVWN5	−9.6	9.6	−3.4	4.7	7.1
G96PWL	−14.2	14.2	−8.4	8.4	11.3
G96VWN5	−14.5	14.5	−8.8	8.8	11.7
mPWPWL	−6.5	6.5	−0.8	4.6	5.6
mPWVWN5	−6.8	6.8	−0.5	4.0	5.4
OPWL	−15.5	15.5	−10.9	10.9	13.2
OVWN5	−15.7	15.7	−11.2	11.2	13.5
PBEPWL	−3.8	4.2	2.1	4.2	4.2
PBEVWN5	−4.1	4.4	2.4	4.5	4.5
TPSSPWL	−11.6	11.6	−5.3	5.3	8.4
TPSSVWN5	−11.8	11.8	−5.6	5.6	8.7
G96HLYP	−10.4	10.4	−3.6	4.9	7.6
		MLBE21/05 + TMAE9/05[c]			
BPWL	−3.2	7.7	0.7	5.7	6.7
BVWN5	−3.4	7.8	0.7	5.9	6.9
G96PWL	−6.8	9.9	−3.1	7.2	8.6
G96VWN5	−7.0	10.1	−3.3	7.4	8.7
mPWPWL	−1.0	6.6	2.7	6.0	6.3
mPWVWN5	−1.2	6.7	2.8	5.7	6.2
OPWL	−8.4	10.7	−5.2	8.2	9.4
OVWN5	−8.6	10.9	−5.4	8.3	9.6
PBEPWL	1.0	5.7	4.9	6.2	6.0
PBEVWN5	0.8	5.7	5.0	6.4	6.1
TPSSPWL	−4.1	8.9	−1.2	5.6	7.2
TPSSVWN5	−4.2	8.9	−1.4	5.6	7.3
G96HLYP	−3.6	8.1	0.6	5.7	6.9

[a] All values in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2. [c] The two data sets are weighted 0.5:0.5, as in Table 5.

PBEPWL has the lowest AMUE in the third section of the table, but B97-2 has the lowest MUE with the TZQ basis set.

Given that we can improve the results by setting $Y = 0$, we initially optimized Y for BLYP, BPBE, BPW91, G96LYP, G96PBE, G96PW91, mPWLYP, mPWPBE, mPWPW91, OLYP, OPBE, OPW91, PBELYP, PBEPBE (also called PBE), and PBEPW91. We optimized Y by minimizing the MUE with the TZQ basis set of the errors for the BEs of Cu2, Cr2, V2, Zr2, $CrCH_3^+$, $Fe(CO)_5$, $NiCH_2^+$, and VS. (Cu_2, Cr_2, V_2, and Zr_2 are the molecules in TMAE4/05 and $CrCH_3^+$, $Fe(CO)_5$, $NiCH_2^+$, and VS are the molecules in MLBE4/05.) The OLYP functional with scaled Y had much larger errors in bond lengths (discussed in the next section) than G96LYP, so only the G96LYP functional with scaled Y is presented here. The optimum value of Y for G96LYP is 50, and the functional is called G96HLYP, which stands for G96 exchange with half-LYP. G96HLYP has an AMUE of 6.1 kcal/mol when tested against MLBE21/05, which is 0.8 kcal/mol larger than the AMUE for TPSS1KCIS. However, G96HLYP has much smaller errors when tested against both MLBE21/05 and TMAE9/05 than does TPSS1KCIS (see Tables 5 and 9). But, as discussed in Section 5.2, TPSS1KCIS is only the 20th best functional in Table 5 when transition metal dimers and metal−ligand bonds are considered together. Table 5 shows that G96LYP and BLYP, with AMUEs of 6.4 and 6.6 kcal/mol, respectively, are the best conventional functionals when transition metal dimers and metal−ligand bond energies are weighted equally. Table 9 shows four additional functionals with AMUEs less than 6.4 kcal/mol for this broad test of functionals for metal binding, namely, PBEPWL (6.0 kcal/mol), PBEVWN5 (6.1 kcal/mol), mPWVWN5 (6.2 kcal/mol), and mPWPWL (6.3 kcal/mol). In fact, all four of these functionals are very similar in form as well as in average error. Thus the GGE-type functional is quite successful for metal bond energies.

6. Bond Lengths

The errors for the bond lengths are given in Table 10. Table 10 contains the errors for the 42 methods that were discussed in Section 4.2 and the errors for the 13 GGE and GGSC discussed in Section 5.5. In our previous work on transition metal-only systems, SPWL and SVWN3 were the methods with the lowest errors when tested against TMBL8/05 (8 bond lengths for transition metal diatomics), whereas SPWL and SVWN3 are the two most inaccurate methods when tested against MLBL13/05. In fact, SPWL and SVWN3 have errors that are about twice as large as the most accurate methods. The methods that are the most accurate when tested against MLBL13/05, using both AMUE and MUE with the TZQ basis set as our criteria, are TPSS1KCIS and TPSSh. The MUEs for TPSS1KCIS/TZQ and TPSSh/TZQ are both 0.010 Å and the AMUEs for TPSS1KCIS/TZQ and TPSSh/TZQ are both 0.013 Å. It is pleasing that one of the recommended methods for bond energies of metal−ligand complexes (TPSS1KCIS) is also one of the most accurate methods for bond lengths. We can also see that the GGE and GGSC tend to have larger AMUEs when tested against MLBL13/04 than the GGA, hybrid GGA, meta GGA, and hybrid meta GGA methods. However, the MUEs for the GGE and GGSC methods with the TZQ basis set are more in accord with the GGA, hybrid GGA, meta GGA, and hybrid meta GGA methods. We note that the new G96HLYP functional also does well for bond lengths.

In Table 11 we present the MSEs, MUEs, and AMUEs averaged over the TMBL8/05 and MLBL13/05 databases. Of the 54 functionals in Table 11, the most accurate methods are BPBE, BP86, PBE, and mPWPW91. The BPBE and PBE methods have the lowest MUEs with the TZQ basis set (0.019 and 0.020 Å, respectively) and BP86 and mPWPW91 have the lowest AMUEs (0.042 Å). The most accurate GGE or GGSC method is G96HLYP, which has an MUE with the TZQ basis set of 0.029 Å and an AMUE of 0.057 Å.

7. Ionization Potentials

The ionization potential database was included because Hertwig and Koch[39] indicated that GGE functionals are inaccurate for ionization potentials and that gradient-corrected correlation functionals are needed for ionization potentials. The errors for all of the methods tested against IP7/05 are given in Table 12. The most accurate methods are B1B95, O3LYP, OLYP, and PBE1PBE (all four of these methods have AMUEs less than 4 kcal/mol). The absolutely best method tested against IP7/05 is OLYP, which has an AMUE of 3.1 kcal/mol. As anticipated above, the GGE methods all do poorly and have

TABLE 10: The Mean Signed Error (MSE), Mean Unsigned Error (MUE), and Average Mean Unsigned Error (AMUE) for the MLBL13/05 Database of Bond Lengths[a]

	DZQ		TZQ		
method	MSE	MUE	MSE	MUE	AMUE[b]
LSDA					
SPWL	−0.018	0.025	−0.030	0.030	0.028
SVWN3	−0.020	0.025	−0.033	0.033	0.029
GGA					
BLYP	0.014	0.024	0.007	0.013	0.019
BP86	0.008	0.021	−0.003	0.013	0.017
BPBE	0.009	0.021	−0.003	0.012	0.017
BPW91	0.009	0.021	−0.002	0.012	0.017
G96LYP	0.013	0.023	0.004	0.012	0.018
HCTH	0.013	0.022	0.001	0.011	0.016
mPWLYP	0.013	0.024	0.005	0.013	0.018
mPWPBE	0.008	0.021	−0.004	0.012	0.016
mPWPW91	0.008	0.021	−0.004	0.012	0.016
OLYP	0.016	0.023	−0.004	0.016	0.019
PBE	0.007	0.020	−0.002	0.010	0.015
XLYP	0.014	0.024	0.006	0.013	0.018
hybrid GGA					
B3LYP	0.007	0.017	−0.003	0.010	0.014
B3P86	−0.002	0.014	−0.013	0.015	0.015
B3PW91	0.003	0.015	−0.009	0.013	0.014
B97-1	0.010	0.019	−0.002	0.014	0.017
B97-2	0.006	0.016	−0.006	0.015	0.015
B98	0.009	0.019	0.001	0.011	0.015
BH&HLYP	0.015	0.020	0.004	0.027	0.024
MPW1K	0.005	0.015	−0.006	0.021	0.018
mPW1PW91	0.002	0.014	−0.009	0.014	0.014
MPW3LYP	0.006	0.016	−0.004	0.011	0.013
O3LYP	0.008	0.017	−0.002	0.011	0.014
PBE1PBE	0.002	0.014	−0.010	0.014	0.014
X3LYP	0.006	0.016	−0.003	0.011	0.013
meta GGA					
BB95	0.011	0.021	−0.002	0.012	0.017
mPWB95	0.010	0.020	−0.001	0.013	0.017
mPWKCIS	0.012	0.023	0.001	0.012	0.017
PBEKCIS	0.013	0.023	0.002	0.012	0.017
TPSS	0.010	0.020	−0.001	0.010	0.015
TPSSKCIS	0.010	0.021	−0.001	0.011	0.016
VSXC	0.014	0.025	0.008	0.013	0.019
hybrid meta GGA					
B1B95	0.002	0.013	−0.010	0.015	0.014
BB1K	0.004	0.012	−0.008	0.019	0.016
MPW1B95	0.001	0.013	−0.011	0.016	0.014
MPW1KCIS	0.007	0.017	−0.002	0.010	0.014
MPWKCIS1K	0.006	0.014	−0.002	0.021	0.018
PBE1KCIS	0.006	0.015	−0.005	0.013	0.014
TPSSh	0.007	0.017	−0.004	0.010	0.013
TPSS1KCIS	0.006	0.016	−0.004	0.010	0.013
GGE					
BPWL	0.022	0.030	0.012	0.019	0.024
BVWN5	0.022	0.029	0.012	0.019	0.024
G96PWL	0.019	0.027	0.008	0.017	0.022
G96VWN5	0.019	0.027	0.008	0.017	0.022
mPWPWL	0.021	0.029	0.011	0.018	0.023
mPWVWN5	0.021	0.029	0.011	0.018	0.023
OPWL	0.021	0.025	0.008	0.014	0.019
OVWN5	0.021	0.025	0.008	0.014	0.019
PBEPWL	0.020	0.027	0.012	0.017	0.022
PBEVWN5	0.020	0.027	0.011	0.017	0.022
TPSSPWL	0.021	0.028	0.011	0.017	0.022
TPSSVWN5	0.021	0.028	0.011	0.016	0.022
GGSC					
G96HLYP	0.016	0.025	0.005	0.014	0.019

[a] All values in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

TABLE 11: The Mean Signed, Mean Unsigned, and Average Mean Unsigned Errors (MSEs, MUEs, and AMUEs, respectively) Averaged over the MLBL13/05 and TMBL8/05 Databases of Bond Lengths, with Each Database Weighted Equally[a]

	DZQ		TZQ		
	MSE	MUE	MSE	MUE	AMUE[b]
LSDA					
SPWL	−0.015	0.034	−0.032	0.048	0.041
SVWN3	−0.018	0.035	−0.038	0.043	0.039
GGA					
BLYP	0.063	0.068	0.020	0.026	0.047
BP86	0.055	0.062	0.007	0.023	0.042
BPBE	0.078	0.084	0.005	0.019	0.052
BPW91	0.072	0.078	0.009	0.023	0.050
G96LYP	0.064	0.069	0.015	0.023	0.046
HCTH	0.086	0.093	0.073	0.085	0.089
mPWLYP	0.055	0.060	0.019	0.025	0.042
mPWPBE	0.073	0.080	0.006	0.021	0.051
mPWPW91	0.069	0.075	0.007	0.022	0.048
OLYP	0.087	0.090	0.055	0.073	0.081
PBE	0.070	0.077	0.007	0.020	0.049
XLYP	0.057	0.063	0.019	0.026	0.044
hybrid GGA					
B3LYP	0.081	0.091	0.061	0.082	0.087
B3P86	0.070	0.087	0.048	0.084	0.086
B3PW91	0.082	0.096	0.060	0.090	0.093
B97-1	0.065	0.082	0.077	0.092	0.087
B97-2	0.061	0.080	0.065	0.087	0.084
B98	0.072	0.091	0.078	0.092	0.092
BH&HLYP	0.126	0.136	0.082	0.126	0.131
MPW1K	0.107	0.127	0.101	0.134	0.131
mPW1PW91	0.085	0.101	0.061	0.095	0.098
MPW3LYP	0.079	0.091	0.060	0.083	0.087
O3LYP	0.085	0.096	0.066	0.087	0.092
PBE1PBE	0.083	0.099	0.060	0.094	0.096
X3LYP	0.080	0.092	0.059	0.084	0.088
meta GGA					
BB95	0.079	0.087	0.061	0.075	0.081
mPWB95	0.082	0.091	0.066	0.080	0.085
mPWKCIS	0.085	0.092	0.069	0.079	0.086
PBEKCIS	0.097	0.103	0.080	0.089	0.096
TPSS	0.078	0.088	0.053	0.066	0.077
TPSSKCIS	0.086	0.094	0.064	0.076	0.085
VSXC	0.081	0.091	0.064	0.076	0.084
hybrid meta GGA					
B1B95	−0.086	0.140	−0.109	0.140	0.140
BB1K	0.041	0.060	0.019	0.055	0.058
MPW1B95	0.048	0.059	0.014	0.047	0.053
MPW1KCIS	0.061	0.070	0.045	0.066	0.068
MPWKCIS1K	0.107	0.117	0.039	0.067	0.092
PBE1KCIS	0.085	0.092	0.011	0.036	0.064
TPSSh	0.068	0.079	0.007	0.029	0.054
TPSS1KCIS	0.073	0.083	0.014	0.036	0.060
GGE					
BPWL	0.093	0.096	0.035	0.039	0.068
BVWN5	0.094	0.098	0.035	0.040	0.069
G96PWL	0.093	0.097	0.031	0.038	0.067
G96VWN5	0.093	0.097	0.030	0.037	0.067
mPWPWL	0.088	0.092	0.033	0.037	0.065
mPWVWN5	0.089	0.093	0.033	0.037	0.065
OPWL	0.109	0.111	0.087	0.095	0.103
OVWN5	0.109	0.111	0.087	0.095	0.103
PBEPWL	0.085	0.089	0.027	0.039	0.064
PBEVWN5	0.086	0.089	0.033	0.038	0.064
TPSSPWL	0.093	0.097	0.036	0.040	0.068
TPSSVWN5	0.093	0.097	0.036	0.040	0.068
GGSC					
G96HLYP	0.079	0.084	0.022	0.029	0.057

[a] All units in Å. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

errors that are roughly double their GGA counterparts. (For example, BLYP has an AMUE of 8.1 kcal/mol and BVWN5 has an AMUE of 17.0 kcal/mol.) The method that performed the best for metal−ligand bonding (TPSS1KCIS) is roughly 1

TABLE 12: The Mean Signed, Mean Unsigned, and Average Mean Unsigned Errors (MSEs, MUEs, and AMUEs, respectively) for the IP7/05 Database of Ionization Potentials[a]

	DZQ		TZQ		
	MSE	MUE	MSE	MUE	AMUE[b]
LSDA					
SPWL	14.2	14.2	11.6	11.6	13.3
SVWN3	24.8	24.8	22.6	22.3	23.6
GGA					
BLYP	9.1	9.1	6.8	7.1	8.1
BP86	12.8	12.8	10.6	10.7	11.8
BPBE	8.8	8.8	6.5	7.1	8.0
BPW91	9.5	9.5	7.1	7.6	8.5
G96LYP	7.6	7.6	5.0	5.8	6.7
HCTH	6.0	6.0	1.8	5.5	5.7
mPWLYP	9.9	9.9	6.6	7.8	8.8
mPWPBE	9.6	9.6	7.2	7.2	8.6
mPWPW91	10.3	10.3	7.8	8.3	9.3
OLYP	0.0	3.3	−2.4	3.0	3.1
PBE	9.1	9.1	7.5	7.8	8.4
XLYP	9.3	9.3	6.8	7.2	8.3
hybrid GGA					
B3LYP	8.1	8.1	3.5	6.3	7.2
B3P86	18.6	18.6	14.9	16.7	17.6
B3PW91	5.6	6.3	1.9	5.3	5.8
B97-1	3.0	3.1	−5.6	5.2	4.2
B97-2	−3.0	4.3	−9.4	7.3	5.8
B98	3.5	3.7	−4.6	4.8	4.2
BH&HLYP	1.4	3.7	−6.9	5.7	4.7
MPW1K	0.3	4.3	−6.6	6.1	5.2
mPW1PW91	3.4	5.2	−0.3	4.3	4.8
MPW3LYP	6.7	7.1	2.3	5.7	6.4
O3LYP	0.2	3.8	−3.2	3.4	3.6
PBE1PBE	2.8	4.7	−0.8	4.0	4.3
X3LYP	6.6	6.6	1.3	5.0	5.8
meta GGA					
BB95	4.1	6.0	5.4	6.0	6.0
MPWB95	5.0	6.4	5.7	5.8	6.1
MPWKCIS	12.9	12.9	10.2	10.9	11.9
PBEKCIS	12.7	12.7	10.5	11.0	11.9
TPSS	5.4	5.9	2.5	5.5	5.8
TPSSKCIS	5.8	6.1	3.4	5.3	5.6
VSXC	2.1	4.7	−2.2	3.8	4.2
hybrid meta GGA					
B1B95	−1.2	3.1	−4.1	4.0	3.6
BB1K	−2.5	3.1	−7.1	5.3	4.2
MPW1B95	−0.6	3.1	−4.4	4.2	3.6
MPW1KCIS	8.6	8.6	5.4	7.6	8.1
MPWKCIS1K	3.4	5.7	−2.7	4.8	5.3
PBE1KCIS	6.8	7.4	3.2	6.3	6.8
TPSSh	2.9	4.2	−0.6	4.4	4.3
TPSS1KCIS	2.6	4.8	−0.4	4.2	4.5
GGE					
BPWL	17.9	17.9	14.4	16.1	17.0
BVWN5	18.0	18.0	14.4	15.9	17.0
G96PWL	16.6	16.6	12.8	14.5	15.5
G96VWN5	16.6	16.6	12.9	14.6	15.6
mPWPWL	18.6	18.6	15.1	16.8	17.7
mPWVWN5	18.8	18.8	15.2	16.9	17.8
OPWL	9.0	9.0	5.3	8.4	8.7
OVWN5	9.2	9.2	5.5	8.6	8.9
PBEPWL	18.5	18.5	15.1	16.7	17.6
PBEVWN5	18.5	18.5	15.3	16.9	17.7
TPSSPWL	13.8	13.8	11.1	13.5	13.7
TPSSVWN5	13.9	13.9	11.2	13.6	13.8
GGSC					
G96HLYP	11.6	11.6	8.6	9.6	10.6

[a] All units in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

kcal/mol worse than the more accurate methods for ionization potentials.

8. New Functionals

The primary purpose of the study reported here is to assess the performance of the many functionals already in the literature for bond energies, ionization potentials, and bond distances relevant to organometallic chemisty, but in the course of our study we made a number of attempts to improve on the functionals in the literature for bond energies, ionization potentials, and bond distances relevant to organometallic chemistry. A mark of how difficult it is to design functionals for metallic chemistry is that none of these attempts yielded functionals significantly better than the best functionals already in the literature, at least when measured across all the data considered. Thus most of these attempts were relegated to the dustbin. So far we have discussed only one new functional, namely G96HLYP. However, it is instructive to describe the two most successful of our new functionals, which are called MOHLYP and MPWLYP1M and which are discussed next.

For energetics, the OLYP method is among the best of the previously developed functionals (for the data considered in the present study), but it has a large error in the Cr_2 bond length. The only nonhybrid methods that do very poorly for this quantity are OLYP and HCTH, which are also the only two nonhybrid methods to violate the uniform electron gas (UEG) limit. The functional form of the gradient enhancement for the OptX exchange functional used in OLYP is

$$F(s) = 1.05151 - \frac{b}{C_F}\frac{\gamma s^2}{(1 + \gamma s^2)} \qquad (12)$$

where $\gamma = 0.006$, $b = 1.4317$, C_F is from the LDA, and s is the reduced gradient. The UEG limit can be restored by adjusting 1.05151 to 1.0, and doing this drastically improves the bond length for Cr_2. However, the quality of most other predictions degrades, especially the atomization energies of main group molecules. We also noticed that the performance of OLYP against many (not all) of the data studied here is improved if we use the half-LYP (HLYP) correlation functional instead of the LYP correlation functional. Therefore we replaced 1.05151 by 1.0 and LYP by HLYP, and we optimized b. The error function against which we optimized b is the mean unsigned error of the 17 data in TMAE4, MLBE4, AE6, and IP3, where IP3 is a database that contains the ionization potentials of Cr, Cu, and O. The TZQ basis set was used during the optimization. The optimized value of b is 1.292, and the resulting exchange potential is called the metal-adjusted OptX or MOptX (also abbreviated MO just as OptX is abbreviated O). Combing MOptX with HLYP is called MOHLYP. The results for the new method are given in the top half of Table 13.

Enforcing the UEG limit improves the bond length for Cr_2, but the other bond lengths get worse, and the net result is a slight increase in the accuracy of the bond lengths and a neglible decrease in the accuracy of the bond energies. The performance of MOHLYP for AE6 is much worse than the performance of OLYP, but the MUEs of AE6 are still smaller than the errors for TMAE9 or MLBE21. Overall, the use of MOHLYP is encouraged for the metal systems where the UEG limit is important.

The final new functional that we present is MPWLYP1M, which denotes MPW exchange, LYP correlation, and one parameter optimized for metals. The parameter is X (the percentage of Hartree−Fock exchange), and it has a value of 5. The performance is shown in the bottom half of Table 13.

TABLE 13: Mean Errors for MOHLYP and MPWLYP1M over Six Databases

	DZQ		TZQ		
database	MSE	MUE	MSE	MUE	AMUE
MOHLYP energetics					
AE6	2.6	2.6	−2.1	2.2	2.4
IP7/05	0.0	3.4	−1.6	2.8	3.0
ML21/05	1.7	5.5	4.0	6.3	5.9
TMAE9/05	−8.1	8.1	−3.9	5.8	7.0
MOHLYP bond lengths					
TMBL8/05	0.172	0.172	0.068	0.073	0.123
MLBL13/05	0.027	0.035	0.013	0.020	0.027
MPWLYP1M energetics					
AE6	0.1	1.0	−0.7	0.9	1.0
IP7/05	7.9	7.9	5.6	6.5	7.2
MLBE21/05	5.8	7.0	7.7	8.2	7.6
TMAE9/05	−5.4	6.9	0.6	2.3	4.6
MPWLYP1M bond lengths					
TMBL8/05	0.118	0.120	0.043	0.054	0.087
MLBL13/05	0.013	0.024	0.004	0.011	0.017

9. Combined Performance on Multiple Databases

In this paper, we have presented three new databases that test the bond energies, bond lengths, and ionization potentials of atomic and metal−ligand systems. It is difficult to recommend only one DFT method because the number of DFT methods is overwhelming, and the methods each have different strengths and weaknesses. Therefore it is useful to identify a small set of functionals that perform well for multiple kinds of data. In Table 14 we average the errors over the AE6, IP7/05, MLBE21/05, and TMAE9/05 databases of energies; in particular, the MUEs are computed as

$$\mathrm{MUE} = (1/4)\mathrm{MUE(AE6)} + (1/4)\mathrm{MUE(IP7)} + (1/4)\mathrm{MUE(TMAE9)} + (1/4)\mathrm{MUE(MLBE21)} \quad (13)$$

where MUE(AE6) is the MUE of AE6, MUE(IP7) is the MUE for IP7/05, and so forth. The MUEs for the MLBE21/05 database are on a per metal−ligand bond basis, as explained in Section 5.2, and the MUEs for AE6 are also per bond.

Notice from Table 14 that the GGE methods, which looked so promising when we compared the MLBE21/05 results in Table 9 to the results in Table 4, are no longer so promising when we look at the performance averaged over four energetic databases. This illustrates our contention that it is necessary to assess functionals against a diverse range of databases. The five methods with the lowest AMUEs when averaged over the four energetic databases, equally weighted as specified in eq 13, and also averaged over the two basis sets, have their AMUE in bold in Table 14. The two methods with the very lowest AMUEs are OLYP and MOHLYP, with errors of 4.4 and 4.6 kcal/mol, respectively.

An even broader assessment is possible by considering both the energetic quantities of Table 14 and the bond lengths of Table 11. Table 15 combines the AMUEs of Table 11 and the AMUEs of Table 14. Only methods that have an AMUE among the ten best in Table 11 or among the ten best of Table 14 (or both) are included in Table 15. The final column of Table 15 is an average unsigned error over the six databases considered in this article, each computed with two basis sets and all weighted equally, except that the mean unsigned errors in the bond lengths are scaled by 5.0 kcal/mol/(0.042 Å) to make the energy scales comparable (as explained in footnote *c* of the table). This composite column then summarizes the most systemic, extensive, and consistent set of tests available for density functionals applied to organometallic chemistry and metal-containing molecules. The six best performing density functionals

TABLE 14: The Mean Unsigned and Average Mean Unsigned Errors (MUEs and AMUEs, respectively) Averaged over the AE6, IP7/05, MLBE21/05, and TMAE9/05 Databases of Energies[a]

	DZQ	TZQ	AMUE[b]
LSDA			
SPWL	19.8	21.2	20.5
SVWN3	24.1	26.0	25.1
GGA			
BLYP	5.5	5.9	5.7
BP86	8.3	8.5	8.4
BPBE	6.5	6.0	6.2
BPW91	6.8	6.0	6.4
G96LYP	5.8	5.0	5.4
HCTH	5.4	6.5	5.9
mPWLYP	5.9	7.0	6.5
mPWPBE	7.0	6.7	6.9
mPWPW91	7.3	6.8	7.1
OLYP	**4.4**	**4.5**	**4.4**
PBE	7.4	7.7	7.6
XLYP	5.7	6.4	6.0
hybrid GGA			
B3LYP	9.3	7.4	8.3
B3P86	11.4	10.2	10.8
B3PW91	9.6	8.2	8.9
B97-1	8.1	5.0	6.6
B97-2	6.2	4.7	5.4
B98	8.3	5.2	6.7
BH&HLYP	16.4	15.5	16.0
MPW1K	14.1	13.4	13.7
mPW1PW91	10.3	9.3	9.8
MPW3LYP	9.1	7.0	8.1
MPWLYP1M	**5.9**	**4.4**	**5.1**
O3LYP	6.9	5.6	6.2
PBE1PBE	9.6	9.1	9.3
X3LYP	8.9	7.4	8.1
meta GGA			
BB95	7.9	7.7	7.8
mPWB95	8.8	9.2	9.0
MPWKCIS	7.2	7.5	7.4
PBEKCIS	7.6	8.2	7.9
TPSS	**5.7**	**5.1**	**5.4**
TPSSKCIS	**5.3**	**5.3**	**5.3**
VSXC	5.9	5.3	5.6
hybrid meta GGA			
B1B95	8.7	8.2	8.5
BB1K	12.0	11.4	11.7
MPW1B95	8.8	8.1	8.4
MPW1KCIS	8.6	7.3	7.9
MPWKCIS1K	14.7	13.2	13.9
PBE1KCIS	9.8	8.4	9.1
TPSSh	6.9	5.5	6.2
TPSS1KCIS	7.4	5.5	6.5
GGE			
BPWL	8.9	7.3	8.1
BVWN5	9.0	7.4	8.2
G96PWL	10.0	7.8	8.9
G96VWN5	10.0	8.0	9.0
mPWPWL	8.4	7.4	7.9
mPWVWN5	8.5	7.3	7.9
OPWL	8.1	6.5	7.3
OVWN5	8.2	6.7	7.4
PBEPWL	7.7	7.5	7.6
PBEVWN5	7.7	7.6	7.7
TPSSPWL	9.0	7.1	8.0
TPSSVWN5	9.0	7.1	8.1
GGSC			
G96HLYP	7.6	5.7	6.6
MOHLYP	**4.9**	**4.3**	**4.6**

[a] All units in kcal/mol. [b] AMUE = [MUE(DZQ) + MUE(TZQ)]/2.

TABLE 15: Average Mean Unsigned Errors on Composite Databases of Energies (in kcal/mol) and Bond Lengths (in Å)

functional	energies[a]	bond lengths[b]	composite[c]
B97-2	5.4	0.084	6.9
BLYP	5.7	0.047	5.7
BP86	8.4	0.042	7.3
BPW91	6.4	0.050	6.3
G96LYP	5.4	0.046	5.4
HCTH	5.9	0.089	7.5
OLYP	4.4	0.081	6.1
MOHLYP	4.6	0.075	6.0
mPWLYP	6.5	0.042	6.0
MPWLYP1M	5.1	0.052	5.5
PBE	7.6	0.049	7.0
SPWL	20.1	0.041	15.0
SVWN3	25.1	0.039	18.3
TPSS	5.4	0.077	6.7
TPSSh	6.2	0.054	6.3
TPSSKCIS	5.3	0.085	6.9
XLYP	6.0	0.044	5.7

[a] 0.25 × MUE(TMAE9/05) + 0.25 × MUE(MLBE21/05) + 0.25 × MUE(AE6) + 0.25 × MUE(IP7/05). [b] 0.5 × MUE(TMBL8/05) + 0.5 × MUE(MLBL13/05). [c] (4 × column 2 + 2 × (5.0 kcal/0.042 Å mol) × column 3)/6, where the factor 4 is the number of databases averaged to obtain column 2, the factor 2 is the number of databases averaged to obtain column 3, 5.0 kcal/mol is the average of the five lowest values in column 2, and 0.042 Å is the average of the five lowest values in column 3.

out of the 57 tested on the six databases considered in this paper are found to be (in rank order, followed by their composite average error, given in kcal/mol) G96LYP (5.4), MPWLYP1M (5.5), XLYP (5.7), BLYP (5.7), MOHLYP (6.0), and mPWLYP (6.0). The popular functional BP86 has a mean error of 7.3, on this scale, and the theoretically well justified functionals PBE and TPSS have mean errors of 6.0 and 6.7, respectively. We recognize that the precise identification of the better performing functionals can depend to some extent on the composition and weighting of individual databases, but we found that all reasonable weightings of the databases gave similar results in the present cases, and that the composite column does a reasonably good job of summarizing the findings of this study. Nevertheless, readers are invited to reanalyze the data presented in this article from their own points of view if that seems appropriate for their own applications. For example, if one computes the B_1 diagnostics, one can choose functionals that work well for molecules of similar types and similar B_1 values, using the theoretical considerations of Section 5.3.

10. Conculsions

A key focus of this paper is metal−ligand bonding, for which we present two databases, and we have also used other databases for ionization potentials and for main-group and transition metal bonding. The most accurate method for metal−ligand bond energies is TPSS1KCIS, but TPSS1KCIS is no longer the most accurate method when the test set is broadened to include the other test sets. The most highly recommended functionals for broadly accurate predictions of energetics and bond lengths of inorganometallic and organometallic compounds are (in ranked order) G96LYP, MPWLYP1M, XLYP, BLYP, MOHLYP, and mPWLYP because they have the best average performance when the errors are averaged over test sets that include main-group, transition metal−transition metal, and metal−ligand bond energies, ionization potentials, and transition metal dimer and metal−ligand bond lengths.

It is interesting that five of the six best performing density functionals have no Hartree−Fock exchange, and the other has only 5% Hartree−Fock exchange. Five years ago, even while making progress on nonhybrid exchange, Becke prognosticated that functionals with Hartree−Fock exchange would "remain the DFTs of first choice for reliability and robustness" even if not for cost.[92] Four years ago, an obituary[105] was published for "pure DFT", which is called nonhybrid DFT in the present article (that is, DFT without Hartree−Fock exchange). In retrospect we can now see that the negative assessment and the premature obituary ("The report of my death was an exaggeration." − Mark Twain) for nonhybrid functionals were a consequence of relying primarily on Pople's heat-of-formation databases,[2,92,106−108] which are skewed heavily toward organic chemistry and nonmetals.[109] We hope that the systematic databases we have presented for metal-containing systems will allow for more broad-based assessment in the future.

As increasing numbers of computational chemists turn their attention to technological problems involving metals, nonhybird DFT should become the method of choice for more applications, at least if one is interested in metallic and metal−ligand bond energies and bond lengths and ionization potentials, which are especially important for oxidation−reduction processes. However, if one broadens the assessment to include barrier heights, noncovalent interactions, and main-group charge-transfer complexes, one finds that the functionals of the types that perform best here are less successful.[4,58,65,70,110−114] The search for a universally successful functional continues.

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Supporting Information Available: A validation of the scale factor that we have used in calculating the zero-point energy and details about how we converted r_0 to r_e, as well as the errors for MLBE4/05 and tables of root-mean-square errors to complement the mean unsigned errors presented in Tables 4, 9, 10, and 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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