Assessment of Density Functional Theory Methods for the Computation of Heats of Formation and Ionization Potentials of Systems Containing Third Row Transition Metals

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The performance of several different density functional theory (DFT) methods, including GGA, hybrid-GGA, meta-GGA, and hybrid-meta-GGA methods, have been assessed in terms of their ability to accurately compute both heats of formation and ionization potentials of systems containing third row transition metals. Two different basis sets were used in this study: 6-31G** and TZVP. It is found that the triple-ζ quality TZVP basis set generally produces the best results for both heats of formation and ionization potentials. One important observation made in this study is that the inclusion of exact exchange terms in DFT methods generally results in more consistently accurate results for both heats of formation and ionization potentials of transition metal systems. In general, DFT methods do not yield good ionization potential results for systems containing titanium or zinc. For heats of formation, it is found that the hybrid-meta-GGA functional, TPSS1KCIS, yields the best overall results when combined with the TZVP basis set, while PBE1PBE (hybrid-GGA) gives the best results for the 6-31G** basis. The hybrid-GGA functional, B3LYP, is found to produce the lowest overall errors for ionization potentials when combined with both 6-31G** and TZVP.

1. Introduction

Transition metals and their complexes play a very important role in chemistry. These elements, for example, are crucial in industrial catalysis, biological catalysis, protein−ligand interactions, and protein structure. It is difficult to treat transition metal complexes using theoretical techniques because of the near degeneracies that occur in these systems due to the partial filling of d orbitals. In order to make very accurate wavefunction based calculations for these systems, it is necessary to use expensive multireference methods such as multireference configuration interaction (MRCI). As there is currently great interest in performing calculations on large systems containing transition metals, it has become necessary to use computational methods that are considerably less expensive than the multireference methods. Density functional theory (DFT) presently offers hope for the accurate determination of the molecular properties of large systems containing transition metals with a single determinant method. In this work we seek to assess the accuracy that can be expected of DFT methods for the calculation of heats of formation and ionization potentials of systems containing third row transition metals.

In this work we consider two important physical properties: the ionization potential and the heat of formation. The ionization potential, the energy required to remove an electron from a bound state to infinite separation, has been known for some time to be an important property of atoms and molecules. The ability to predict ionization potentials accurately has significant implication for the field of photoelectron spectroscopy. The heat of formation is the change in enthalpy that occurs when a molecule is formed from its constituent elements in their most stable states. This physical parameter is used to assess the stability of a molecule, to estimate the amount of energy released in a reaction, and to calculate other thermodynamic properties.

Because the exact density functional is unknown, most DFT methods comprise a correlation functional, an exchange functional and, in some cases, an exact exchange term, of the same form as HF exchange in order to approximate the exact density functional. Therefore, DFT is not a single method but a family of methods. Some recently developed functionals also contain terms that are functionally dependent on the kinetic energy density. Generally, density functional methods can be divided into five classes according to the types of functional dependencies that they possess. The simplest type of DFT is the local spin-density approximation (LSDA), which depends only on electron density. Generalized gradient approximation (GGA) functionals depend on the electron density and its reduced gradient, while meta-GGA functionals also depend on the kinetic energy density. Hybrid and hybrid-meta functionals are combinations of GGA and meta-GGA functionals with Hartree−Fock exchange. Examples of GGA, hybrid-GGA, meta-GGA, and hybrid-meta-GGA are examined in this study. Table 1 lists all of the functionals investigated in this work and indicates the category to which each functional belongs.

TABLE 1: Various Functionals Employed in this Study

functional	type	refs
BLYP	GGA	31, 32
MPWPW91	GGA	33−35
PBEPBE	GGA	36
B3LYP	hybrid-GGA	31, 32, 37, 38
PBE1PBE	hybrid-GGA	36, 39, 40
B98	hybrid-GGA	41
TPSSTPSS	meta-GGA	42, 43
TPSSKCIS	meta-GGA	42−46
BB95	meta-GGA	31, 47
B1B95	hybrid-meta-GGA	31, 47
TPSS1KCIS	hybrid-meta-GGA	42−46, 48
BB1K	hybrid-meta-GGA	31, 47, 49

Perdew and Schmidt’s “Jacob’s ladder” approach for the systematic improvement of density functional approximations contains five rungs, with each possessing more accurate approximations than the one below it.[1] The four classes of density functionals investigated in this work contain elements

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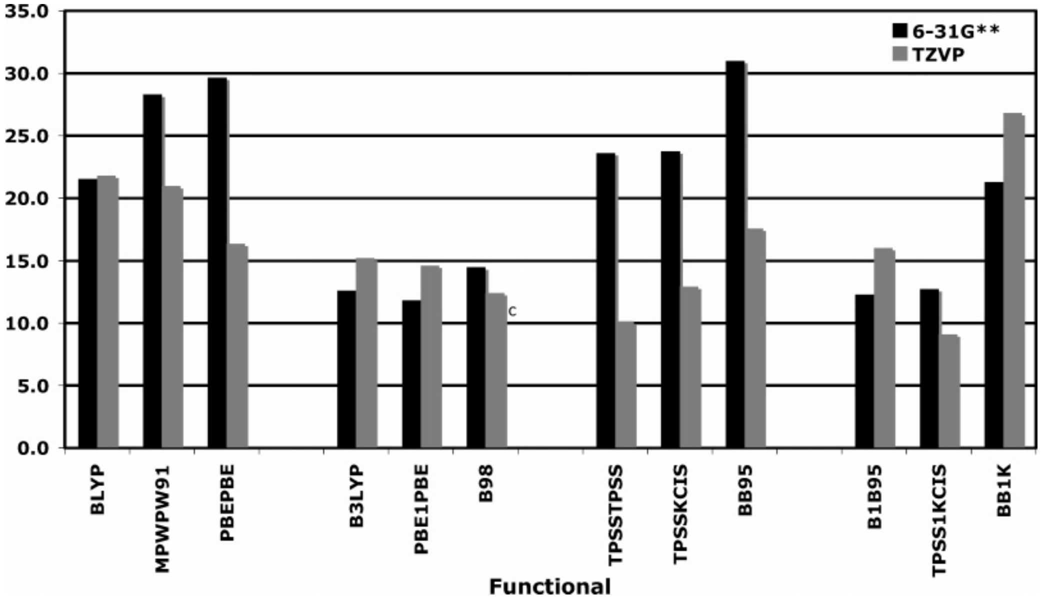

Figure 1. Average unsigned heat of formation errors for the entire set of transition metal systems considered in this work.

of the second, third, and fourth rung of "Jacob's ladder", with the hybrid-meta-GGA functionals being the most complex. Functionals residing on the highest rung in this scheme would include both an exact exchange term and an "exact partial correlation" term.[1,2] There have been a limited number of fifth rung functionals developed in the past few years, bet they are not widely used. An example of a fifth rung functional is that of Perdew and co-workers that combines exact exchange and second-order correlation with a gradient-corrected density functional.[3,4] Since the use of functionals in this work is confined to more widely used DFT methods, functionals from the fifth rung of "Jacob's ladder" are not included here. We have also excluded members of the first rung of functionals, namely the LSDA functionals, which depend functionally only on the electron density. This is done because of extreme difficulties in getting LSDA calculations to converge properly and because there is significant evidence that these functionals perform poorly for transition metal systems. Truhlar and co-workers have shown that LSDA functionals give very poor results for bond energies and ionization potentials,[5] while Görling and co-workers observed that SVWN, an LSDA functional, produces very high errors for metal-carbonyl dissociation energies.[6]

In this work we have employed two different basis sets, 6-31G**[7] and TZVP.[8,9] The Pople type split valence basis sets are the most extensively used basis sets in chemistry and are very well validated, in this study we utilize 6-31G**, a double-ζ Pople type basis set with polarization functions on all atoms. TZVP is a triple-ζ basis set that uses a single Gaussian contraction to describe inner shells and three basis functions to describe outer shells. Both of these basis sets are used throughout chemistry and have been widely utilized, along with density functional methods, for studies of transition metal systems (for examples see refs 10−14).

The two test sets utilized in this study consisted of 94 heats of formation and 58 ionization potentials for atomic and molecular systems containing third row transition metals. For all of these systems, the most recent available experimental data are used. It should be noted that scandium has been omitted from our tests because, for heats of formation, the experimental atomic enthalpy of formation is unavailable, but it is necessary for the calculation of molecular heats of formation. Tables 2 and 3 give the experimental values for heats of formation and ionization potentials respectively.

There have been several studies carried out within the past few years that seek to assess the performance of DFT methods in describing properties of systems containing transition metals.[5,6,15−24] Furche and Perdew evaluated the performance of several different density functional methods for the description of bond energetics, molecular structures, dipole moments, and harmonic frequencies of transition metal systems;[15] this work was carried out using a quadruple-ζ quality basis set.[25] Cundari et al. evaluate the accuracy with which heats of formation of molecules containing transition metals can be computed with the B3LYP functional combined with the, pseudopotential based, LANL2DZ and CEP-31G(d) basis sets.[16] Glukhovtsev, Bach, and Nagel studied bond dissociation energies, ionization potentials, enthalpies of formation, and harmonic frequencies of iron containing compounds using the B3LYP functional along with an "in house" pseudopotential based basis set.[17] All of these prior studies provide interesting insights in their own right, so the work described herein extend these important works by thoroughly comparing a series of transition metals with a consistent choice of functionals combined with standard basis sets. While the present work provides important new insights, it also should be viewed as a starting point for the development of accurate and rigorously validated functionals that can be used routinely to study the properties of transition metal systems.

2. Methods

All calculations were carried out using the Gaussian 03 suite of programs.[26] Heats of formation were calculated using the method specified in "Thermochemistry in Gaussian" white paper available at http://www.Gaussian-.com/g_whitepap/thermo.htm.[27] Values for ionization potentials were calculated adiabatically.

At this point it is worth describing the philosophy of this work. Our main interest is to estimate the accuracy that can be expected of DFT methods for the prediction of heats of formation and ionization potentials of larger systems. In order to carry out this assessment, we compute the values of these properties for small systems, for which experimental data are

TABLE 2: Experimental Heats of Formation for All Molecules Considered in this Work (kcal/mol)

TiH	116.4 ± 2.3[a]	MnH	64.2 ± 7.0[b]	Ni_2	156.7[l]
TiO	13.7 ± 2.2[b]	MnO	29.6 ± 3.0[b]	NiH	85.6 ± 2.6[b]
TiN	112.1 ± 7.0[b]	MnOH	3.7 ± 3.2[b]	NiO	75.0 ± 5.0[b]
TiF	−4.0 ± 8.0[b]	MnF	−19.9 ± 3.0[b]	NiF	17.5[b]
TiF_2	−164.5 ± 10.0[c,d]	MnF_2	−126.2 ± 1.0[b]	NiF_2	−77.8 ± 1.1[b]
TiF_3	−284.1 ± 10.0[c,d]	MnF_3	−188.0 ± 14.0[b]	NiCl	41.7 ± 1.6[l]
TiCl	24.2[b]	MnCl	11.3 ± 2.1[b]	$NiCl_2$	−17.4 ± 1.0[l]
$TiCl_2$	−57.0 ± 3.0[b]	$MnCl_2$	−63.0 ± 0.5[b,c]	NiS	81.7 ± 5.0[b]
$TiCl_3$	−128.9[c,d,e]	MnS	63.3 ± 2.0[b]	$Ni(OH)_2$	−60.8 ± 3.0[b]
TiS	76.2 ± 2.2[b]			NiCO	35.1 ± 5.8[j]
		Fe_2	172.4 ± 8.0[b]	$Ni(CO)_2$	−39.0 ± 2.5[j]
V_2	187.4 ± 5.2[b]	FeH	117.2 ± 1.0[f]	$Ni(CO)_3$	−92.7 ± 1.9[d]
VH	125.9 ± 2.0[f]	FeO	61.1 ± 3.0[b]	$Ni(CO)_4$	−144.0 ± 0.6[c,d]
VO	30.5[c,g]	FeF	11.4[d]		
VN	121.0 ± 3.0[b]	FeF_2	−93.0 ± 3.4[g]	Cu_2	113.8 ± 2.6[b]
VF	0.7 ± 15.0[b]	FeF_3	−196.2 ± 5.0[g]	CuH	65.9 ± 2.0[b]
VCl	37.8 ± 1.5[b]	FeCl	49.5 ± 1.6[k]	CuO	76.5 ± 10.0[b]
VCl_2	−51.6 ± 3.6[b]	$FeCl_2$	−32.8 ± 1.0[k]	CuOH	28.7 ± 4.0[b]
VCl_3	−88.2 ± 2.1[b]	$FeCl_3$	−60.6 ± 1.0[b]	CuCl	19.3 ± 2.0[b]
VS	80.4 ± 3.2[b]	FeS	83.8 ± 5.0[b]	$CuCl_2$	−9.0[m]
		$Fe(OH)_2$	−79.0 ± 0.5[g]	CuF	−3.2 ± 2.0[b]
CrH	80.2 ± 10.0[b]	Fe(CO)	63.9 ± 3.5[j]	CuF_2	−66.0[b]
CrO	45.0[c,d,e]	$Fe(CO)_2$	0.2 ± 4.9[j]	CuS	75.1 ± 5.0[b]
CrO_2	−18.0[c,d,e]	$Fe(CO)_3$	−55.8 ± 7.6[j]		
CrO_3	−70.5 ± 20.0[b]	$Fe(CO)_4$	−105.1 ± 3.4[d]	Zn_2	57.7 ± 1.5[b]
CrOH	18.9 ± 1.8[h]	$Fe(CO)_4H_2$	−131.0[d]	ZnH	62.9 ± 0.5[b]
$Cr(OH)_2$	−78.1 ± 2.6[h]			ZnO	52.8 ± 0.9[b]
CrN	120.7[e,g]	CoH	110.7 ± 1.0[f]	ZnF_2	−118.9 ± 1.1[b]
CrF	3.1 ± 2.4[i]	CoO	7.0 ± 5.1[b]	ZnCl	6.5 ± 1.0[b]
CrF_2	−99.1 ± 4.2[b]	CoF_2	−87.5[b]	$ZnCl_2$	−63.5 ± 0.4[b]
CrF_3	−199.8 ± 3.4[h]	CoCl	50.3 ± 1.6[k]	ZnS	48.7 ± 3.0[b]
CrCl	31.0 ± 0.6[h]	$CoCl_2$	−22.6 ± 1.0[k]	$Zn(CH_3)$	26.0 ± 2.5[b]
$CrCl_2$	−28.1 ± 0.4[h]	$CoCl_3$	−39.1[c,d,e]	$Zn(CH_3)_2$	12.9 ± 2.0[b]
$CrCl_3$	−67.7 ± 1.5[h]				
CrS	78.2 ± 5.1[b]				

[a] Reference 50. [b] Reference 51. [c] Reference 52. [d] Reference 53. [e] Reference 54. [f] Reference 19. [g] Reference 55. [h] Reference 56. [i] Reference 57. [j] Reference 58. [k] Reference 59. [l] Reference 60. [m] Reference 21.

available, and compare these values to those determined by experiment. Because our main goal is to estimate the performance of DFT methods for larger systems, we have employed only standard methods in this study, that is to say, default grid sizes, convergence criteria, and optimization procedures have been used. This approach seems reasonable because the use of special techniques, such as very fine grids and very tight convergence criteria, is often expensive. Indeed, in several test calculations we have found that finer grids and tighter convergence criteria have little effect on the outcome of most calculations. It should be noted that single point energy calculations on atoms for the computation of heats of formation were calculated using the *tight* keyword in Gaussian.

Previous studies have used molecular geometries obtained at high levels of theory for the calculation of molecular properties at lower levels of theory. Because information based on high levels of theory is not available for larger molecules, we feel that it is more appropriate to optimize the molecular geometry using the same basis set and density functional that is being evaluated for a given molecular property. We have done this for all of the calculations in this work. As DFT methods do not always predict the same spin states as higher level methods, such as MRCI, we have carried out calculations for all of the systems considered in this work at several different spin multiplicities (2, 4, 6, and 8 for even multiplicity systems and 1, 3, 5, and 7 for odd multiplicity systems). The spin state with the lowest electronic energy for any given system is used for the computation of both heats of formation and ionization potentials (please see Supporting Information for calculated multiplicities of each system for all functional/basis combinations).

3. Results and Discussion

Heats of Formation. Figure 1 gives the average unsigned heat of formation errors for each of the 94 systems considered in this work as calculated with all twelve functionals used in this study along with both the 6-31G** and TZVP basis sets. Not entirely unexpectedly, it can be seen that the larger, TZVP, basis set produces the lowest unsigned heat of formation errors for seven of the twelve functionals tested here. It is interesting to note that, for all three meta-GGA functionals, the TZVP basis outperforms the 6-31G** basis by a significant margin.

The hybrid-GGA and hybrid-meta-GGA functionals, always produce the lowest heat of formation errors when they are paired with the 6-31G** basis set. It should be noted however that the BB1K/6-31G** method yields errors that are only slightly lower than those of BLYP/6-31G**. The best overall result for this basis set corresponds to an average unsigned error of 11.8 kcal/mol and is given by the PBE1PBE functional.

For the TZVP basis, there is no clear pattern for the relationship between functional class and the quality of the heat of formation results, although it can be said that the GGA functionals, which contain neither exact exchange nor kinetic energy density terms, generally produce higher errors than the other methods. As in the case of the 6-31G** basis, the BB1K/TZVP method produces disappointing results. With an average unsigned error value of 9.1 kcal/mol, the TPSS1KCIS functional yields the lowest overall average heat of formation errors for the TZVP basis set.

Tables 4 and 5 give the average unsigned and signed heat of formation errors (respectively) for systems containing the various transition metals considered in this work. Considering

TABLE 3: Experimental Ionization Potentials for All Sytems Considered in this Work (eV)

TiH	6^{a}	$FeCl_2$	10.63 ± 0.10^{c}
TiO	6.819 ± 0.006^{a}	Fe(CO	6.66 ± 0.17^{d}
TiF_2	12.2 ± 0.5^{a}	$Fe(CO)_2$	6.68 ± 0.24^{d}
TiF_3	10.5 ± 0.5^{a}	$Fe(CO)_3$	7.25 ± 0.35^{d}
TiS	7.1 ± 0.3^{a}	$Fe(CO)_4$	8.48^{a}
V_2	6.357 ± 0.001^{a}	CoH	7.86 ± 0.07^{a}
VO	7.2386 ± 0.0006^{a}	CoO	8.9 ± 0.2^{a}
VN	8.0 ± 1.0^{a}	CoCl	8.71 ± 0.10^{c}
VS	8.4 ± 0.3^{a}	$CoCl_2$	10.75 ± 0.10^{c}
CrOH	7.54 ± 0.05^{b}	NiH	8.50 ± 0.10^{a}
CrO	8.16 ± 0.01^{a}	NiO	9.5 ± 0.2^{a}
CrO_2	10.3 ± 0.5^{a}	NiF_2	11.5 ± 0.3^{a}
CrO_3	11.6 ± 0.5^{a}	NiCl	9.28 ± 0.10^{c}
CrF	9.3 ± 0.4^{a}	$NiCl_2$	11.24 ± 0.01^{a}
CrF_2	10.6 ± 0.3^{a}	Ni(CO)	7.30 ± 0.29^{d}
CrF_3	12.5 ± 0.3^{a}	$Ni(CO)_2$	7.79 ± 0.22^{d}
CrCl	8.50 ± 0.10^{c}	$Ni(CO)_3$	7.69 ± 0.25^{d}
$CrCl_2$	9.9^{a}	$Ni(CO)_4$	8.722 ± 0.010^{a}
MnH	7.8^{a}	Cu_2	7.9^{a}
MnO	8.65 ± 0.20^{a}	CuF	10.90 ± 0.01^{a}
MnF	8.51 ± 0.20^{a}	CuF_2	13.18^{a}
MnF_2	11.38 ± 0.20^{a}	CuCl	10.7 ± 0.3^{a}
MnF_3	12.57 ± 0.20^{a}		
MnCl	8.5 ± 0.3^{c}	Zn_2	9.0 ± 0.2^{a}
$MnCl_2$	11.03 ± 0.01^{a}	ZnH	9.4^{a}
		ZnO	9.34 ± 0.02^{e}
Fe_2	6.3^{a}	ZnF_2	13.91 ± 0.03^{a}
FeO	8.9 ± 0.2^{a}	$ZnCl_2$	11.80 ± 0.005^{a}
FeF_2	11.3 ± 0.3^{a}	$Zn(CH_3)$	7.2^{a}
FeF_3	12.5 ± 0.3^{a}	$Zn(CH_3)_2$	9.4^{a}
FeCl	8.08 ± 0.10^{c}		

[a] Reference 53. [b] Reference 59. [c] Reference 51. [d] Reference 57. [e] Reference 61. [f] Reference 58. [g] Reference 62. [h] Reference 63.

TABLE 4: Average Unsigned Heat of Formation Errors for Systems Containing the Various Transition Metal Elements Treated in this Study

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	total
					6-31G**					
BLYP	13.2	14.1	36.1	12.4	22.8	24.3	21.3	31.8	11.0	21.6
MPWPW91	14.6	18.4	50.3	17.3	32.7	24.1	31.1	35.0	15.0	28.3
PBEPBE	17.8	18.4	47.0	17.5	36.7	25.7	35.3	35.5	16.2	29.7
B3LYP	10.2	23.6	14.4	9.0	12.3	7.3	12.0	13.8	8.9	12.6
PBE1PBE	9.3	20.5	12.7	4.9	11.8	7.4	12.9	14.4	10.5	11.8
B98	10.8	19.3	20.9	11.0	11.9	11.6	15.3	17.4	9.3	14.5
TPSSTPSS	14.4	13.2	39.3	14.3	19.7	30.3	26.4	33.8	17.1	23.6
TPSSKCIS	15.3	14.3	39.9	14.3	22.6	19.3	29.8	32.1	15.1	23.8
BB95	18.6	20.2	47.2	17.4	38.6	27.3	39.3	37.1	15.5	31.0
B1B95	9.8	18.4	14.9	6.9	13.1	4.6	14.0	14.3	9.8	12.3
TPSS1KCIS	9.6	10.6	22.0	5.8	8.8	7.8	12.7	21.7	11.7	12.7
BB1K	16.9	38.7	14.9	13.4	32.0	9.9	33.5	11.4	8.8	21.3
					TZVP					
BLYP	13.5	13.6	10.0	8.7	47.1	22.2	43.6	6.1	12.6	21.8
MPWPW91	12.4	10.6	9.3	41.9	23.4	29.4	47.3	5.1	6.2	21.0
PBEPBE	13.2	13.2	9.8	14.1	27.1	28.2	26.1	5.5	6.3	16.4
B3LYP	13.6	18.1	16.8	9.9	19.5	9.9	19.1	10.5	12.6	15.2
PBE1PBE	14.1	22.2	25.5	6.6	16.7	6.8	12.7	9.9	8.0	14.6
B98	14.3	16.9	15.6	12.5	9.6	7.7	15.1	6.7	10.6	12.4
TPSSTPSS	11.2	9.2	6.6	11.2	14.0	32.5	4.7	4.3	6.4	10.1
TPSSKCIS	11.1	10.5	8.0	11.3	35.4	10.0	8.3	4.8	6.0	12.9
BB95	13.2	14.0	11.6	13.8	33.3	23.2	26.9	5.5	7.6	17.6
B1B95	16.0	21.5	26.8	9.1	19.3	8.1	13.9	9.6	9.9	16.0
TPSS1KCIS	10.7	13.4	15.3	4.0	8.8	4.8	6.4	7.0	7.7	9.1
BB1K	24.6	31.6	37.6	16.1	37.0	17.0	34.8	12.8	10.7	26.8

the 6-31G** basis set, there are several types of transition metal systems that prove to be particularly problematic for these DFT methods, these are chromium, nickel, and copper. The worst results were obtained for systems containing chromium, only four of the twelve functionals, the hybrid-GGA B3LYP and PBE1PBE functionals and the hybrid-meta-GGA B1B95 and BB1K functionals, produce average unsigned errors lower than 20.0 kcal/mol for these systems. All of the GGA and meta-GGA functionals produce average errors greater than 35.0 kcal/mol for chromium systems. It is interesting to note that, with the 6-31G** basis set, all of the GGA functionals produce average errors greater than 20.0 kcal/mol for systems containing chromium, iron, cobalt, nickel, and copper. Similarly, the meta-GGA methods produce average errors greater than 20.0 kcal/mol for systems containing chromium, nickel, and copper. B1B95 is the only functional considered in this work that yields an average unsigned error smaller than 20.0 kcal/mol for each of the transition metal system types studied in this work.

In Table 5 it can be seen that, for the 6-31G** basis set, all of the GGA and meta-GGA functionals produce positive average signed heat of formation errors for all types of transition metal systems, indicating a tendency for these methods to underestimate heats of formation (error = experiment-theory). In contrast, most of the hybrid-GGA and hybrid-meta-GGA functionals tend to overestimate heats of formation for all systems except for those containing chromium, copper, and zinc.

For the TZVP basis set, there are no particular types of transition metal systems that are very problematic for all of the DFT methods considered here. It should be noted, however, that all of the GGA functionals produce high errors (bigger than 20.0 kcal/mol) for systems containing iron, cobalt, and nickel.

Among the functionals that produce the best all around results are B3LYP (hybrid-GGA), B98 (hybrid-GGA), and TPSS1KCIS (hybrid-meta-GGA), which all produce heat of formation errors lower than 20.0 kcal/mol for each type of transition metal system. TPSS1KCIS gives average errors lower than 15.0 kcal/mol for all of the transition metal systems with the exception of the chromium systems, for which this functional yields an average unsigned error of 15.4 kcal/mol.

Table 5 shows that, for the TZVP basis set, the GGA and meta-GGA functionals underestimate the heats of formation of most of the transition metal systems. All of the hybrid-GGA and hybrid-meta-GGA methods, with the exception of B98 for iron systems, tend to overestimate the heats of formation of each type of transition metal system. Notably, the heats of formation of systems containing zinc are overestimated by all density functional methods considered here, while only two functionals (BLYP and BB95) underestimate the heats of formation of systems containing chromium.

Table 6 gives the average unsigned heat of formation errors for all of the transition metal coordinating groups considered in this study. Here it can be seen that the types of systems for which density functional methods generally give poor results are the transition metal dimers, the transition metal oxides, and the transition metal carbonyl complexes. For both the 6-31G** and TZVP basis sets, most density functionals give relatively good results for transition metal hydrides and chlorides.

For the 6-31G** basis set, one of the most salient aspects of these data is that all of the GGA and meta-GGA functionals give average errors larger than 25.0 kcal/mol for systems coordinated by nitrogen, oxygen, or carbonyl groups. BLYP is the only functional without exact exchange that produces an average unsigned error lower than 25.0 kcal/mol for systems coordinated by fluorine. The carbonyl coordinating group proved to be particularly problematic for functionals that do not incorporate an exact exchange term, with several methods yielding errors larger than 50.0 kcal/mol, the largest average error for these systems (84.4 kcal/mol) is obtained with the BB95 functional. It is interesting to note that all of the functionals that incorporate exact exchange terms yield errors

TABLE 5: Average Signed Heat of Formation Errors for Systems Containing the Various Transition Metal Elements Treated in this Study

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	total
					6-31G**					
BLYP	7.2	3.8	36.1	6.2	19.6	24.3	17.3	31.8	7.9	18.0
MPWPW91	11.6	15.8	50.3	14.2	32.7	24.1	29.3	35.0	14.4	27.1
PBEPBE	16.5	15.9	47.0	14.3	36.7	25.7	33.5	35.5	16.1	28.7
B3LYP	−7.9	−22.3	14.2	−6.8	−11.3	4.4	−6.9	12.6	3.8	−2.4
PBE1PBE	−6.2	−18.7	11.7	−3.6	−11.3	7.3	−7.6	13.0	7.4	−1.5
B98	−10.5	−19.1	20.9	−9.7	−10.3	−7.7	−13.8	16.7	4.7	−2.8
TPSSTPSS	10.9	9.0	39.3	12.1	19.4	30.3	26.4	33.8	17.1	22.6
TPSSKCIS	11.9	9.4	39.9	11.6	22.5	18.9	29.8	32.1	14.8	22.6
BB95	17.1	17.1	47.2	14.1	38.6	27.3	38.3	37.1	14.4	29.9
B1B95	−7.3	−17.0	8.4	−6.2	−12.8	−2.1	−10.6	13.3	5.5	−3.6
TPSS1KCIS	0.7	−5.9	22.0	1.7	−1.0	4.8	4.7	21.7	10.2	6.8
BB1K	−16.9	−37.9	−7.7	−13.4	−31.8	−9.9	−32.6	3.1	2.9	−17.5
					TZVP					
BLYP	3.4	4.0	3.0	2.7	47.1	22.2	43.6	−1.5	−12.6	15.1
MPWPW91	4.8	1.4	−0.4	41.9	21.0	29.4	47.3	0.4	−6.0	15.8
PBEPBE	7.5	7.0	−3.1	−11.2	25.7	28.2	26.1	2.3	−4.2	12.3
B3LYP	−11.9	−15.2	−16.8	−9.9	−18.0	−9.9	−19.1	−9.9	−12.6	−14.5
PBE1PBE	−11.9	−20.5	−25.5	−6.6	−15.1	−6.8	−12.7	−9.9	−8.0	−14.0
B98	−13.1	−13.7	−15.6	−12.5	6.1	−7.2	−15.1	−5.7	−10.6	−9.4
TPSSTPSS	1.7	1.4	−3.1	9.0	9.7	32.5	2.5	0.6	−3.3	4.4
TPSSKCIS	3.5	2.7	−0.8	8.9	35.1	10.0	5.2	−0.5	−5.6	7.7
BB95	7.7	6.9	5.7	11.1	32.7	23.2	26.9	2.9	−6.2	13.5
B1B95	−13.9	−19.7	−26.8	−9.1	−18.2	−8.1	−13.9	−9.4	−9.9	−15.4
TPSS1KCIS	−5.8	−10.5	−15.3	−1.0	−3.9	−0.2	−5.1	−6.5	−7.5	−6.7
BB1K	−24.5	−30.1	−37.6	−16.1	−36.9	−17.0	−34.8	−12.8	−10.7	−26.6

TABLE 6: Unsigned Heat of Formation Errors for Various Transition Metal Coordinating Groups (MD Denotes Metal Dimers, # Refers to the Number of Examples of a Particular Coordinating Group within the Test Set)

	#	BLYP	MPWPW91	PBEPBE	B3LYP	PBE1PBE	B98	BB95	TPSS	TPSSKCIS	B1B95	TPSS1KCIS	BB1K
						6-31G**							
MD	5	16.4	15.8	16.0	32.3	36.2	27.5	19.5	14.9	13.0	37.8	22.2	62.9
H	9	9.3	10.6	9.9	6.3	6.7	7.7	9.9	11.4	8.5	11.2	8.3	12.5
N	3	31.7	39.5	40.6	8.0	6.1	11.4	42.2	29.3	33.8	7.1	14.5	19.5
O	11	39.5	46.6	47.2	14.9	8.6	14.0	50.2	37.0	37.5	8.0	15.9	19.5
S	8	10.8	18.5	19.0	10.6	14.2	11.0	20.5	17.2	17.1	12.3	7.6	17.9
F	19	24.2	29.5	29.8	14.7	13.4	17.4	31.1	27.1	26.5	13.5	16.6	15.3
Cl	23	12.4	17.3	18.1	10.3	10.0	14.2	17.8	19.0	16.4	10.0	9.6	14.9
OH	6	18.4	27.1	27.4	11.5	9.4	15.1	28.3	19.5	19.6	10.8	13.1	13.7
CO	8	44.9	68.8	79.8	9.7	8.6	12.1	84.4	37.2	51.1	9.8	10.2	51.6
CH3	2	15.2	17.9	19.6	15.9	16.7	16.6	18.3	22.1	18.0	15.8	16.9	14.8
						TZVP							
MD	5	39.8	21.8	15.4	21.8	27.7	13.1	20.3	6.0	15.6	27.9	11.0	48.4
H	9	19.6	15.4	12.1	9.2	8.9	9.9	12.0	12.4	12.0	9.1	9.2	9.9
N	3	17.8	13.2	17.5	9.9	22.0	11.4	19.5	6.7	12.4	18.8	5.5	39.4
O	11	24.9	24.2	21.8	11.8	17.2	16.9	24.6	12.6	15.3	21.2	9.1	39.6
S	8	18.4	19.3	12.9	12.2	11.0	11.0	14.1	10.3	13.2	15.0	8.3	17.1
F	19	14.7	17.4	9.7	14.6	15.9	12.8	10.2	9.5	9.2	16.3	10.8	24.6
Cl	23	14.9	13.9	9.6	15.3	9.3	10.2	9.7	9.1	8.2	10.2	6.6	15.7
OH	6	14.3	18.6	9.2	16.0	18.3	11.4	9.8	11.0	10.6	18.2	13.4	25.9
CO	8	56.0	59.6	58.6	27.4	20.0	15.4	62.1	10.4	33.7	23.1	9.1	59.8
CH3	2	22.4	12.0	13.1	18.2	13.0	18.3	14.3	13.6	11.5	17.8	12.3	18.5

higher than 25.0 kcal/mol for the metal dimers while functionals without exact exchange all produce errors smaller than 20.0 kcal/mol for these types of systems. It is also noteworthy that all of the functionals considered here yield errors lower than 15.0 kcal/mol for the transition metal hydrides.

With respect to the TZVP basis set (in Table 6), the most prominent aspect of these data is that, with this basis, most of the DFT methods produce large average errors for transition metal dimers and for transition metal carbonyl complexes. As in the case of the 6-31G** basis set, the functionals that do not contain exact exchange generally produce extremely poor results for the carbonyl complexes, with the BB95/TZVP method yielding an average unsigned error of 62.1 kcal/mol for these compounds. It should be mentioned that the TPSSTPSS functional, which does not include exact exchange, predicts a reasonably good average heat of formation for carbonyl compounds (10.4 kcal/mol). All functionals yield average errors lower than 15.0 kcal/mol for transition metal hydrides with the exceptions of BLYP (19.6 kcal/mol) and MPWPW91 (15.4 kcal/mol), while only B3LYP (15.3 kcal/mol) and BB1K (15.7 kcal/mol) produce errors higher than 15.0 kcal/mol for transition metal chloride compounds.

Table 7 gives the average unsigned heat of formation errors for all of the systems studied in this work as a function of the number of coordinating groups associated with the transition metal (please note that transition metal dimers are neglected in this analysis).

For the 6-31G** basis set, there are two interesting trends regarding the quality of a functional's predicted heat of formation in relation to the degree of transition metal coordina-

TABLE 7: Unsigned Heat of Formation Errors for Transition Metal Complexes Based on the Number of Coordinating Groups Present (# Refers to the Number of Examples for Each Case; Please Note That Metal Dimers are Omitted in this Analysis)

	#	BLYP	MPWPW91	PBEPBE	B3LYP	PBE1PBE	B98	BB95	TPSS	TPSSKCIS	B1B95	TPSS1KCIS	BB1K
							6-31G**						
1	51	15.8	19.9	20.0	10.2	8.9	12.4	21.3	17.4	16.9	10.0	9.7	14.6
2	24	24.6	32.2	33.7	13.9	14.4	17.2	34.3	29.4	28.5	13.6	15.6	20.2
3	12	33.8	48.0	52.3	12.8	9.7	14.1	53.8	36.6	39.0	9.8	15.3	27.5
4	2	70.2	108.1	126.1	8.5	7.6	4.1	129.5	56.1	78.5	7.1	16.6	65.2
							TZVP						
1	51	19.2	18.5	13.1	10.0	9.8	10.7	14.3	9.8	11.8	11.5	6.9	17.5
2	24	20.7	19.1	13.8	17.8	15.5	13.0	14.6	9.9	11.0	16.6	10.2	27.1
3	12	20.8	25.0	23.9	25.0	25.6	17.2	24.6	13.2	15.4	26.2	14.3	47.2
4	2	61.7	79.9	85.5	42.2	28.8	19.1	88.0	12.2	43.7	33.4	15.8	84.7

tion. For the GGA and meta-GGA functionals, there is a clear pattern in which the heat of formation errors increase with an increasing degree of coordination. With the exception of BB95 (21.3 kcal/mol), all of these methods produce average errors lower than 20.0 kcal/mol for one-coordinated compounds but for the four-coordinated systems yield very high errors (higher than 55.0 kcal/mol). This trend is also seen for BB1K (hybrid-meta-GGA). It is also interesting to note that, with the exception of BLYP for two-coordinated systems (24.6 kcal/mol), none of the GGA or meta-GGA methods produce average errors lower than 25.0 kcal/mol for any systems with two or more coordinating groups. For the hybrid-GGA functionals, as well as B1B95 (hybrid-meta-GGA) the two-coordinated systems always exhibit the largest heat of formation errors, these errors decrease as the number of coordinating groups increases past two. B3LYP, PBE1PBE, and B1B95 are the only functionals to produce heat of formation errors lower than 15.0 kcal/mol for all degrees of coordination considered here.

For the TZVP basis set, the trend of increasing error with increasing degree of coordination is exhibited in all but two cases (TPSSTPSS, three-coordinated to four-coordinated; TPSSKCIS one-coordinated to two-coordinated). B98, TPSSTPSS, and TPSS1KCIS are the only three functionals to produce errors lower than 20.0 kcal/mol for four-coordinated complexes while all of the GGA functionals give very high errors for these compounds (at least 61.7 kcal/mol). The only functional that yields errors lower than 15.0 kcal/mol for all degrees of coordination is TPSSTPSS.

It is interesting to compare these heat of formation results for transition metal systems with results obtained for standard organic compounds, Riley et al. have recently performed a study evaluating the performance of a wide variety of density functional methods and basis sets for the computation of several atomic and molecular properties.[28] In this study the 6-31G* basis set was utilized, this basis is identical to 6-31G** except that polarization functions on hydrogen are omitted. It was found that, for the twelve functionals considered in this work, the average unsigned heat of formations errors for organic systems follow a trend very similar to that of the transition metal systems. The DFT heat of formation computations for the organic complexes are generally more accurate than those for transition metal compounds, typically yielding errors about six to twelve kcal/mol lower. Methods including exact exchange yield the best results for both organic and transition metal systems, while GGA functionals produce the highest errors for both types of compounds.

Ionization Potentials. Figure 2 gives the average unsigned ionization potential errors for each of the 58 systems used in this study as calculated with all twelve functionals considered in this work along with both the 6-31G** and TZVP basis sets. One of the most interesting aspects of these data is that, for both basis sets, five of the six methods that include exact exchange produce errors that are lower than all of the methods that do not have exact exchange terms. The BB1K (hybrid-meta-GGA) outperforms the GGA and meta-GGA methods when used with the 6-31G** basis set, but produces the highest ionization potential errors for the TZVP basis. It can also be seen in this figure that, for each of the functionals, TZVP outperforms 6-31G** by a significant margin.

TABLE 8: Average Unsigned Ionization Potential Errors for Systems Containing the Various Transition Metal Elements Treated in this Study

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	total
					6-31G**					
BLYP	1.58	0.59	1.36	1.43	1.08	0.69	0.67	1.73	1.28	1.16
MPWPW91	1.55	0.53	1.18	1.32	0.95	0.70	0.76	1.61	1.20	1.08
PBEPBE	1.58	0.54	1.24	1.36	0.98	0.73	0.76	1.73	1.21	1.12
B3LYP	1.44	0.70	0.74	0.94	0.75	0.60	0.46	1.44	1.03	0.85
PBE1PBE	1.47	0.77	0.80	0.91	0.84	0.66	0.68	1.33	1.10	0.92
B98	1.56	0.64	1.14	0.97	0.64	0.87	0.61	1.30	1.14	0.95
TPSSTPSS	1.56	0.69	1.24	1.40	0.96	0.85	0.72	1.87	1.32	1.15
TPSSKCIS	1.59	0.67	1.29	1.44	0.98	0.86	0.76	1.86	1.33	1.18
BB95	1.68	0.67	1.39	1.50	1.03	0.83	0.75	1.79	1.29	1.20
B1B95	1.52	1.03	0.75	0.99	0.88	0.79	0.96	1.38	1.17	1.01
TPSS1KCIS	1.51	0.59	1.22	1.19	0.96	0.83	0.67	1.75	1.27	1.09
BB1K	1.89	1.22	0.79	0.80	0.95	0.82	1.02	1.26	1.06	1.04
					TZVP					
BLYP	1.41	0.39	0.77	0.98	0.59	0.55	0.48	0.66	0.98	0.75
MPWPW91	1.41	0.37	0.64	0.87	0.56	0.55	0.51	0.60	0.89	0.70
PBEPBE	1.37	0.37	0.68	0.95	0.59	0.57	0.53	0.65	0.93	0.73
B3LYP	1.13	0.32	0.31	0.51	0.42	0.39	0.30	0.35	0.74	0.48
PBE1PBE	1.33	0.38	0.34	0.50	0.50	0.55	0.36	0.48	0.81	0.56
B98	1.32	0.73	0.51	0.58	0.69	0.56	0.39	0.46	0.86	0.66
TPSSTPSS	1.28	0.44	0.74	0.94	0.50	0.54	0.46	0.77	1.02	0.73
TPSSKCIS	1.36	0.44	0.76	0.97	0.52	0.54	0.50	0.77	1.04	0.76
BB95	1.42	0.42	0.82	0.99	0.61	0.58	0.56	0.67	0.99	0.79
B1B95	1.57	0.32	0.44	0.55	0.70	0.56	0.49	0.42	0.88	0.65
TPSS1KCIS	1.23	0.38	0.58	0.74	0.39	0.59	0.31	0.67	0.97	0.63
BB1K	1.50	0.69	0.49	0.43	0.93	0.59	1.21	0.62	0.80	0.82

The hybrid-GGA functionals generally produce the best ionization potential results, for the 6-31G** basis these functionals outperform all others, the lowest overall unsigned error for 6-31G** is 0.85 eV and is obtained with B3LYP. For the TZVP basis set, two of the three hybrid-GGA functionals, B3LYP and PBE1PBE, outperform all other functionals while B98 yields errors that are higher than those of B1B95 and TPSS1KCIS (both hybrid-meta-GGA functionals). The best overall result for TZVP is obtained with the B3LYP functional and corresponds to an average error of 0.48 eV.

Table 8 gives the average unsigned ionization potential errors for compounds containing the various transition metals studied in this work. Here it can be seen that, for both the 6-31G** and TZVP basis sets, density functional methods yield poor results for systems containing titanium. For the 6-31G** basis, the best results for these systems correspond to an average error of 1.44 eV (B3LYP); for the TZVP basis, the lowest error obtained is 1.13 eV (B3LYP).

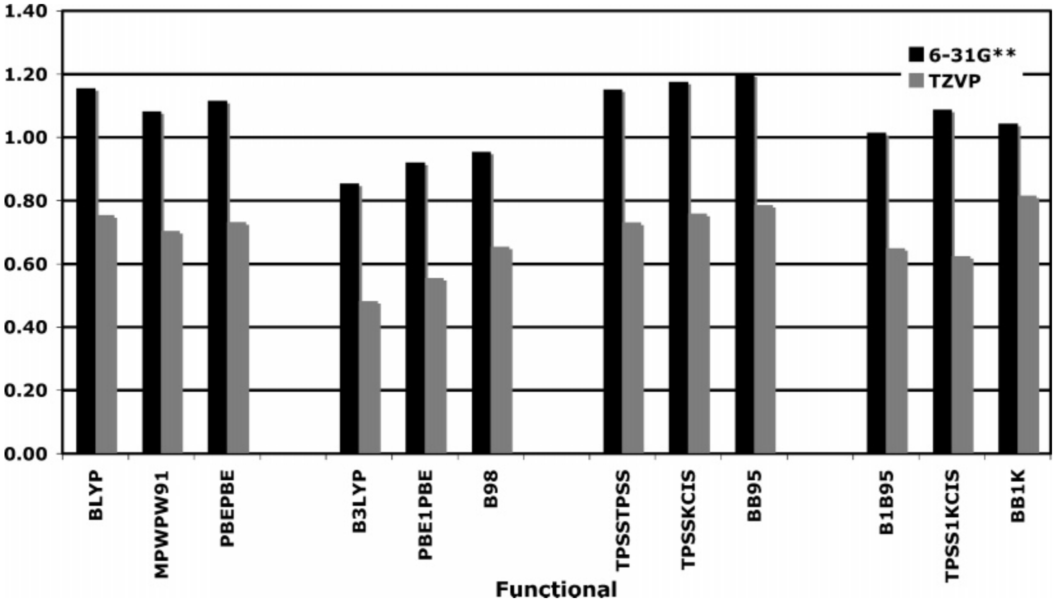

Figure 2. Average unsigned ionization potential errors for the entire set of transition metal systems considered in this work.

Considering only the 6-31G** basis set, it seems apparent that these DFT methods give better results for systems in higher spin states, all methods yield very poor results for systems that tend to have low multiplicities, namely those containing titanium, copper, and zinc. It should also be noted that these functionals also produce high errors for systems containing chromium and manganese; for these systems, functionals containing no exact exchange terms yield very high errors (greater than 1.15 eV). Generally the best results are obtained for systems containing cobalt and nickel, with the hybrid-GGA functionals producing the lowest average errors for these systems.

For the TZVP basis set, the highest unsigned ionization potential errors are obtained for systems containing titanium and zinc, the systems that tend to have the lowest multiplicity among those considered here. The lowest errors are generally produced for systems containing vanadium, cobalt, and nickel; all functionals, with the exceptions of B98 and BB1K, produce average unsigned errors lower than 0.60 eV for all of these types of systems. As was the case for the 6-31G** basis, the hybrid-GGA class of functionals yields the best results for ionization potentials, with the B3LYP and PBE1PBE functionals producing errors lower than 0.60 eV for all transition metal systems types, excluding those containing titanium and zinc.

Table 9 gives signed ionization potential errors for each type of transition metal system studied here. These data indicate that, for both basis sets, these DFT methods generally underestimate ionization potentials. Indeed, for the 6-31G** basis, every functional produces a positive average signed error for each of the transition metal types. For the TZVP basis, there are only four entries in Table 9 with negative values, these are B1B95 (vanadium), MPWPW91 (nickel), PBEPBE (nickel), and BB95 (nickel).

TABLE 9: Average Signed Ionization Potential Errors for Systems Containing the Various Transition Metal Elements Treated in this Study

	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	total
					6-31G**					
BLYP	1.44	0.59	1.36	1.43	0.85	0.69	0.45	1.73	1.28	1.07
MPWPW91	1.38	0.53	1.18	1.32	0.71	0.70	0.39	1.61	1.20	0.97
PBEPBE	1.41	0.54	1.24	1.36	0.73	0.73	0.41	1.73	1.21	1.01
B3LYP	1.04	0.70	0.67	0.94	0.65	0.60	0.34	1.44	1.03	0.77
PBE1PBE	1.12	0.77	0.38	0.91	0.81	0.66	0.55	1.33	1.10	0.80
B98	1.26	0.64	0.98	0.97	0.46	0.87	0.33	1.30	1.14	0.83
TPSSTPSS	1.56	0.69	1.24	1.40	0.87	0.85	0.48	1.87	1.32	1.10
TPSSKCIS	1.50	0.67	1.29	1.44	0.90	0.86	0.54	1.86	1.33	1.12
BB95	1.56	0.67	1.39	1.50	0.81	0.83	0.44	1.79	1.29	1.11
B1B95	1.24	0.58	0.67	0.99	0.87	0.79	0.63	1.38	1.17	0.89
TPSS1KCIS	1.38	0.51	1.22	1.19	0.96	0.83	0.60	1.75	1.27	1.06
BB1K	0.52	0.75	0.48	0.80	0.86	0.43	0.48	1.26	1.06	0.72
					TZVP					
BLYP	0.99	0.36	0.77	0.95	0.28	0.37	0.01	0.66	0.98	0.58
MPWPW91	0.95	0.29	0.62	0.79	0.22	0.38	−0.09	0.60	0.89	0.49
PBEPBE	1.04	0.31	0.68	0.88	0.26	0.41	−0.06	0.65	0.93	0.54
B3LYP	0.80	0.19	0.18	0.51	0.33	0.28	0.09	0.35	0.73	0.37
PBE1PBE	0.71	0.30	0.20	0.43	0.41	0.55	0.22	0.48	0.81	0.43
B98	0.90	0.73	0.51	0.58	0.63	0.56	0.25	0.46	0.86	0.59
TPSSTPSS	1.23	0.43	0.74	0.91	0.32	0.54	0.06	0.77	1.02	0.63
TPSSKCIS	1.13	0.42	0.76	0.94	0.35	0.54	0.10	0.77	1.04	0.64
BB95	1.19	0.42	0.82	0.96	0.30	0.43	−0.03	0.67	0.99	0.61
B1B95	1.08	−0.06	0.17	0.53	0.61	0.48	0.36	0.42	0.88	0.50
TPSS1KCIS	1.06	0.37	0.58	0.74	0.39	0.59	0.17	0.67	0.97	0.59
BB1K	1.00	0.14	0.08	0.35	0.69	0.54	0.58	0.62	0.80	0.52

Table 10 gives the average unsigned ionization potential errors for each of the coordinating groups considered in this study as calculated with all functional/basis combinations. Here it can be seen that, for both basis sets, the functionals considered here generally give disappointing results for compounds containing nitrogen and fluorine. B3LYP stands out as the best functional for producing consistently good results; for the 6-31G** basis set, this functional gives errors no higher than 1.00 eV for all types of systems except the metal dimers (1.41 eV) and systems containing fluorine (1.53 eV). For the TZVP basis, B3LYP produces errors higher than 0.70 eV only for compounds containing fluorine (0.80 eV) and nitrogen (0.80 eV).

For the 6-31G** basis set, the worst results are obtained for transition metal systems coordinated by fluorine, with all functionals yielding errors higher than 1.50 eV; it should be noted that the GGA and meta-GGA functionals all produce errors higher than 2.00 eV for these systems. The metal dimers also proved to be quite problematic for these DFT methods; only one of the functionals gives an average error lower than 1.20 eV, and B98/6-31G** produces an average error of 0.82 eV for these systems. The methods containing no exact exchange terms yield errors no lower than 1.00 eV for systems coordinated by chlorine, while only the GGA functionals and B3LYP produce errors lower than 1.00 eV for systems containing

TABLE 10: Unsigned Ionization Potential Errors for Various Transition Metal Bonding Partners (MD Denotes Metal Dimers; # Refers to the Number of Examples of a Particular Bonding Partner within the Test Set)

	#	BLYP	MPWPW91	PBEPBE	B3LYP	PBE1PBE	B98	BB95	TPSS	TPSSKCIS	B1B95	TPSS1KCIS	BB1K
							6-31G**						
MD	4	1.43	1.20	1.20	1.41	1.66	0.82	1.23	1.42	1.37	1.70	1.61	1.83
H	5	0.88	0.94	0.96	0.86	0.97	1.01	0.93	1.01	1.03	1.10	1.09	1.15
N	1	1.00	0.96	0.97	0.91	1.03	1.28	1.13	1.14	1.11	1.18	1.12	1.20
O	10	0.59	0.54	0.56	0.46	0.57	0.77	0.66	0.70	0.72	0.69	0.72	0.79
S	2	0.40	0.29	0.30	0.84	1.00	0.15	0.48	0.41	0.42	0.96	0.17	1.33
F	14	2.17	2.08	2.13	1.53	1.50	1.62	2.26	2.13	2.17	1.55	1.86	1.26
Cl	12	1.17	1.02	1.08	0.59	0.63	0.79	1.24	1.10	1.14	0.76	0.94	0.82
OH	1	0.90	0.74	0.77	0.38	0.51	0.68	0.90	0.90	0.90	0.70	0.79	0.62
CO	7	0.35	0.46	0.46	0.37	0.46	0.53	0.36	0.27	0.30	0.55	0.45	0.93
CH3	2	0.71	0.54	0.56	0.46	0.46	0.57	0.68	0.64	0.68	0.56	0.62	0.50
							TZVP						
MD	4	0.42	0.45	0.46	0.62	0.92	0.79	0.48	0.64	0.64	0.94	0.79	1.16
H	5	0.77	0.79	0.73	0.69	0.82	0.60	0.71	0.62	0.70	0.83	0.74	0.88
N	1	0.87	0.82	0.84	0.80	0.94	1.17	0.98	1.00	0.97	0.76	1.01	1.13
O	10	0.29	0.30	0.30	0.24	0.32	0.67	0.34	0.36	0.36	0.50	0.40	0.71
S	2	0.30	0.17	0.20	0.06	0.55	0.72	0.37	0.26	0.28	0.42	0.09	0.49
F	14	1.32	1.21	1.30	0.80	0.78	0.91	1.37	1.31	1.34	0.85	1.05	0.85
Cl	12	0.89	0.75	0.80	0.45	0.41	0.52	0.89	0.78	0.85	0.55	0.57	0.73
OH	1	0.25	0.07	0.12	0.03	0.05	0.23	0.23	0.22	0.23	0.16	0.19	0.15
CO	7	0.50	0.60	0.59	0.19	0.39	0.36	0.57	0.37	0.38	0.52	0.22	1.07
CH3	2	0.50	0.35	0.38	0.33	0.32	0.41	0.49	0.46	0.50	0.42	0.46	0.39

TABLE 11: Unsigned Ionization Potential Errors for Transition Metal Complexes Based on the Number of Coordinating Groups Present (# Refers to the Number of Examples for Each Case; Please Not That Metal Dimers are Omitted in this Analysis

	#	BLYP	MPWPW91	PBEPBE	B3LYP	PBE1PBE	B98	BB95	TPSS	TPSSKCIS	B1B95	TPSS1KCIS	BB1K
							6-31G**						
1	29	0.79	0.75	0.78	0.70	0.77	0.88	0.85	0.90	0.90	0.87	0.86	0.99
2	17	1.58	1.47	1.51	0.98	1.05	1.12	1.64	1.43	1.49	1.16	1.36	1.02
3	7	1.64	1.59	1.64	0.91	0.86	0.91	1.71	1.56	1.59	0.89	1.16	0.81
4	1	0.15	0.13	0.10	0.59	0.65	1.12	0.00	0.00	0.08	0.84	0.45	1.43
							TZVP						
1	29	0.51	0.47	0.48	0.36	0.46	0.57	0.52	0.50	0.52	0.58	0.49	0.75
2	17	1.13	1.02	1.08	0.66	0.65	0.83	1.18	1.03	1.09	0.73	0.81	0.89
3	7	1.13	1.13	1.16	0.44	0.48	0.49	1.22	1.10	1.12	0.52	0.67	0.60
4	1	0.10	0.16	0.15	0.62	0.70	0.72	0.03	0.03	0.05	0.92	0.47	1.55

nitrogen. The GGA and meta-GGA methods all yield good results for compounds coordinated by sulfur and carbonyl groups, these methods give errors lower than 0.50 eV for these systems.

Considering the TZVP basis set, the only types of systems that proved to be particularly problematic are those that contain either fluorine or nitrogen. All of the functionals considered here, with the exception of B1B95 (0.76 eV), give errors that are higher than 0.80 eV for all systems containing nitrogen. Only PBE1PBE (0.78 eV) produces errors lower than 0.80 eV for fluorine systems; it is also interesting to note that all of the GGA and meta-GGA methods yield errors greater than 1.00 eV for these compounds. Interestingly, the best results for metal dimers are obtained with the GGA functionals, and BLYP gives the best result with an error of 0.42 eV. These DFT methods all produce very good results for transition metals coordinated by hydroxyl groups, with all functionals yielding errors lower than 0.30 eV.

Table 11 gives the average unsigned ionization potential errors for all of the systems studied in this work as a function of the number of coordinating groups associated with the transition metal (please note that transition metal dimers are neglected in this analysis).

There is an interesting trend among the functionals that do not include an exact exchange term for the 6-31G** basis set. For these functionals, the unsigned ionization potential errors increase as the degree of coordination increases from one to three, and dramatically decrease for the four-coordinated systems. The GGA and meta-GGA functionals produce very high errors (greater than 1.40 eV) for two-coordinated and three-coordinated compounds, reasonable errors (0.75−0.90 eV) for one-coordinated systems, and very low errors (less than 0.15 eV) for four-coordinated molecules. For the functionals containing exact exchange terms, the ionization potential errors increase as the degree of coordination increases from one to two and then generally decrease as the degree of coordination increases from two to four. This trend applies to all of the functionals except for B98 and BB1K for which the four-coordinated systems have higher errors than the three-coordinated ones.

For the TZVP basis, the trend exhibited by the GGA and meta-GGA functionals is the same as with 6-31G**. For these functionals with no exact exchange terms, the errors for the two-coordinated and three-coordinated systems are significantly lower for TZVP than for 6-31G** (between 1.02 and 1.22 eV). For the functionals with exact exchange terms, the one-coordinated and three-coordinated complexes generally have the lowest errors while the two-coordinated and four-coordinated systems have higher errors. This trend is true for all hybrid-GGA and hybrid-meta-GGA functionals with the exception of TPSS1KCIS (hybrid-meta-GGA), for which the four-coordinated systems exhibit the lowest average unsigned error.

As was done for the case of heats of formation, we will now compare the 6-31G** transition metal results to the 6-31G* organic system results obtained by Riley et al. for ionization potentials. The most striking difference between the two sets of data is that the errors obtained for transition metal systems are larger than those for organic complexes by a large margin, transition metal errors are in the range between 0.85 and 1.20 eV, while the errors for organic systems are between 0.25 and 0.35 eV. As evidenced by the narrow range of ionization potential errors for organic compounds, there is very little difference in the quality of any particular type of functional for these systems, this contrasts the results for transition metal complexes for which gradient corrected methods generally produce superior results. It is interesting to note that the hybrid-GGA functional, B3LYP, gives the lowest ionization potential errors for both the organic and transition metal systems.

4. Conclusions

In terms of heats of formation, the TZVP basis set generally produces results that are more accurate and consistent than those of 6-31G** for transition metal systems. It can also be said that, while there is no strong tendency for one functional class to be better than another in terms of overall performance, functionals containing exact exchange tend to yield more consistently good results for the various types of transition metal systems and coordinating groups. The hybrid-GGA and hybrid-meta-GGA functionals generally yield poor results for transition metal dimers compared to their "non-exact-exchange" counterparts. It is also interesting that the inclusion of the kinetic energy density seems to improve the accuracy with which heats of formation are calculated for methods without exact exchange terms but not for functionals with exact exchange.

For the 6-31G** basis set, PBE1PBE (hybrid-GGA) produces the lowest average unsigned heat of formation error of 11.8 kcal/mol. This functional produces errors lower than 21.0 kcal/mol for each type of transition metal system and also yields errors no higher than 20.0 kcal/mol for each type of coordinating group, except transition metal dimers (36.2 kcal/mol).

For the TZVP basis, the functional yielding the lowest overall heat of formation error of 9.1 kcal/mol is TPSS1KCIS (hybrid-meta-GGA), which also produces errors no higher than 16.0 kcal/mol for any particular type of transition metal system. TPSS1KCIS also gives errors lower than 15.0 kcal/mol for each type of coordination group considered here. Interestingly, the BB1K (hybrid-meta-GGA) functional produces disappointing heat of formation results for both the 6-31G** and TZVP basis sets.

In terms of ionization potentials, the TZVP basis always outperforms the 6-31G** basis set for any given functional, generally by about 0.30−0.40 eV. For both basis sets, the inclusion of exact exchange results in an increase in accuracy for ionization potential calculation (this is true for all methods except BB1K/TZVP). The meta-GGA functionals, which include a kinetic energy density term, produce results similar to those of the GGA functionals, while the hybrid-meta-GGA functionals tend to yield higher errors than the hybrid-GGA functionals.

For both the 6-31G** and TZVP basis sets, B3LYP (hybrid-GGA) gives the lowest unsigned ionization potential errors with values of 0.85 and 0.48 eV (respectively). When used along with the TZVP basis set, this functional produces average errors no higher than 0.80 eV for all types of transition metal systems except Ti (1.13 eV). B3LYP also gives errors lower than 0.70 eV for each type of coordinating group, with the exception of nitrogen (0.80 eV) and fluorine (0.80 eV).

Finally, one disappointing result found in this study is that, at least for the 6-31G*(*) basis, DFT methods give much larger heat of formation and ionization potential errors for transition metal compounds than for organic ones. For heats of formation, the functionals tested here generally give average unsigned errors for transition metal systems that are higher than those of organic compounds by about six to twelve kcal/mol. The disparity between the ionization potential results for transition metal and organic complexes is even larger, with errors for the former being about three to four times greater than those of the latter.

Validating the ability of quantum mechanical methods for transition metals continues to be a very challenging task. This is due in part to the electronic nature of transition metals themselves, but the dearth of accurate thermochemical data is a major impediment to making significant progress. This can be alleviated by a renewed experimental effort to generate data of this type, but the use of very sophisticated electronic structure methods like couple-cluster theory can help to fill in some of the gaps in our understanding of transition metal systems. Improvements in functionals continue to advance, but our results show that this does not necessarily translate into significant improvements in the model. Ex post facto corrections can be applied, for example, utilizing the localized orbital model of Friesner and co-workers,[29,30] but while this is a powerful approach, it is less "theoretically satisfying" than having an accurate quantum chemical model.

In the future, we believe that it would be valuable to assess the performance of DFT methods for the computation of atomic and molecular properties of transition metal systems with several more functionals and basis sets. It would be particularly interesting to determine the accuracy that can be expected from density functional techniques when they are used in conjunction with basis sets that incorporate pseudopotentials, which would both lower the computational cost of these calculations and allow for the use of larger valence basis functions.

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Supporting Information Available: Additional information, including heat of formation and ionization potential data for all functional/basis combinations. This material can be found free of charge on the Internet at http://pubs.acs.org.

References and Notes

(1) Perdew, J. P.; Schmidt, K. *AIP Conf. Proc.* **2001**, *577*, 1.

(2) Mattsson, A. E. *Science* **2002**, *298*, 759.

(3) Seidl, M.; Perdew, J. P.; Kurth, S. *Phys. Rev. Lett.* **2000**, *84*, 5070.

(4) Seidl, M.; Perdew, J. P.; Kurth, S. *Phys. Rev. A* **2000**, *62*, art. no.

(5) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 11127.

(6) Görling, A.; Trickey, S. B.; Gisdakis, P.; Rösch, N. *A Critical Assessment of Density Functional Theory with Regard to Applications in Organometallic Chemistry*; Springer-Verlag: Berlin 1999; Vol. 4.

(7) Hehre, W. J.; Ditchfie, R.; Pople, J. a. *J. Chem. Phys.* **1972**, *56*, 2257.

(8) Schafer, a.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(9) Schafer, a.; Huber, C.; Ahlrichs, R. *J. Chem. Phys.* **1994**, *100*, 5829.

(10) Atanasov, M.; Comba, P.; Daul, C. A. *J. Phys. Chem. A* **2006**, *110*, 13332.

(11) Bonifassi, P.; Ray, P. C.; Leszczynski, J. *Chem. Phys. Lett.* **2006**, *431*, 321.

(12) Rusanova, J.; Rusanov, E.; Gorelsky, S. I.; Christendat, D.; Popescu, R.; Farah, A. A.; Beaulac, R.; Reber, C.; Lever, A. B. P. *Inorg. Chem.* **2006**, *45*, 6246.

(13) Zampella, G.; Greco, C.; Fantucci, P.; De Gioia, L. *Inorg. Chem.* **2006**, *45*, 4109.

(14) Zuilhof, H.; Morokuma, K. *Org. Lett.* **2003**, *5*, 3081.

(15) Furche, F.; Perdew, J. P. *J. Chem. Phys.* **2006**, *124*, 044103.

(16) Cundari, T. R.; Leza, H. A. R.; Grimes, T.; Steyl, G.; Waters, A.; Wilson, A. K. *Chem. Phys. Lett.* **2005**, *401*, 58.

(17) Glukhovtsev, M. N.; Bach, R. D.; Nagel, C. J. *J. Phys. Chem. A* **1997**, *101*, 316.

(18) Bach, R. D.; Shobe, D. S.; Schlegel, H. B.; Nagel, C. J. *J. Phys. Chem.* **1996**, *100*, 8770.

(19) Barone, V.; Adamo, C. *Int. J. Quantum Chem.* **1997**, *61*, 443.

(20) Barone, V.; Adamo, C.; Mele, F. *Chem. Phys. Letters* **1996**, *249*, 290.

(21) Wang, S. G.; Schwarz, W. H. E. *J. Chem. Phys.* **1998**, *109*, 7252.

(22) Schwarz, W. H. E.; Wang, S. G.; Scheurer, P. *Abstr. Pap. Am. Chem. Soc.* **2000**, *220*, U501.

(23) Schultz, N. E.; Zhao, Y.; Truhlar, D. G. *J. Phys. Chem. A* **2005**, *109*, 4388.

(24) Zhao, Y.; Truhlar, D. G. *J. Chem. Phys.* **2006**, *124*, 224105.

(25) Weigend, F.; Furche, F.; Ahlrichs, R. *J. Chem. Phys.* **2003**, *119*, 12753.

(26) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Chesseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Forseman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; AlLoham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*; Gaussian Inc.: Wallingford, CT, 2003.

(27) Ochterski, J. W. Themochemistry in Gaussian 2000.

(28) Riley, K. E.; Op't Holt, B. T.; Merz, K. M. *Journal of Chemical Theory and Computation* **2007**, *3*, 407.

(29) Friesner, R. A.; Knoll, E. H.; Cao, Y. *J. Chem. Phys.* **2006**, *125*, 124107.

(30) Knoll, E. H.; Friesner, R. A. *J. Phys. Chem. B.* **2006**, *110*, 18787.

(31) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(32) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(33) Perdew, J. P.; Chevary, J. a.; Vosko, S. H.; Jackson, K. a.; Pederson, M. R.; Singh, D. J.; Fiolhais, C. *Phys. Rev. B* **1992**, *46*, 6671.

(34) Perdew, J. P.; Wang, Y. *Phys. Rev. B* **1992**, *45*, 13244.

(35) Adamo, C.; Barone, V. J. *J. Chem. Phys.* **1998**, *108*, 664.

(36) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(37) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623.

(38) Hertwig, R. H.; Koch, W. *Chem. Phys. Lett.* **1997**, *268*, 345.

(39) Adamo, C.; Barone, V. *Chem. Phys. Lett.* **1998**, *298*, 113.

(40) Adamo, C.; Barone, V. *J. Chem. Phys.* **1999**, *110*, 6158.

(41) Schmider, H. L.; Becke, A. D. *J. Chem. Phys.* **1998**, *108*, 9624.

(42) Staroverov, V. N.; Scuseria, G. E.; Tao, J.; Perdew, J. P. *J. Chem. Phys.* **2003**, *119*, 12129.

(43) Tao, J.; Perdew, J. P.; Staroverov, V. N.; Scuseria, G. E. *Phys. Rev. Lett.* **2003**, *91*, 146401.

(44) Rey, J.; Savin, A. *Int. J. Quantum Chem.* **1998**, *69*, 581.

(45) Krieger, J. B.; Chen, J.; Iafrate, G. J.; Savin, A. In *Electron Correlations and Materials Properties*; Gonis, A., Kioussis, N., Eds.; Plenum: New York 1999; p 463.

(46) Toulouse, J.; Savin, A.; Adamo, C. *J. Chem. Phys.* **2002**, *117*, 10465.

(47) Becke, A. D. *J. Chem. Phys.* **1996**, *104*, 1040.

(48) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *Phys. Chem. Chem. Phys.* **2005**, *7*, 43.

(49) Zhao, Y.; Lynch, B. J.; Truhlar, D. G. *J. Phys. Chem. A* **2004**, *108*, 2715.

(50) Chen, Y. M.; Clemmer, D. E.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *95*, 1228.

(51) Yungman, V. S. Wiley: New York, 1999; Vol. 4−6.

(52) Barin, I. VCH: Weinheim 1989.

(53) Mallard, W. G.; Linstrom, P. J. *NIST Chemistry WebBook*; NIST Standard Reference Database Number 69; National Institute of Standards and Technology: Gaitherburg, MD, 2000.

(54) Binnewies, M.; Milke, E. Wiley-VCH: Weinheim, Germany, 1999.

(55) Chase, M. W.; Davies, C. A.; Downey, J. R.; Frurip, D.; J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; 1985; Vol. 14, Supp. No. 1.

(56) Ebbinghaus, B. B. *Combust. Flame* **1995**, *101*, 311.

(57) Espelid, O.; Borve, K. J. *J. Phys. Chem. A* **1997**, *101*, 9449.

(58) Sunderlin, L. S.; Wang, D. N.; Squires, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 2788.

(59) Hildenbrand, D. L.; LAU, K. H. *J. Chem. Phys.* **1995**, *102*, 3769.

(60) Morse, M. D. *Chem. Rev.* **1986**, *86*, 1049.

(61) Rohlfing, E. a.; Cox, D. M.; Kaldor, a.; Johnson, K. H. *J. Chem. Phys.* **1984**, *81*, 3846.

(62) Lide, D. *CRC Handbook of Chemistry and Physics*; CRC: Boca Raton, FL, 1991.

(63) Clemmer, D. E.; Dalleska, N. F.; Armentrout, P. B. *J. Chem. Phys.* **1991**, *95*, 7263.