

## Regular article

# The electron affinities of transition metal atoms at the CCSD(T) and density functional levels of theory

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**Abstract.** The electron affinities of Ti, V, Cr, Fe, Co, Ni, and Cu are computed using the density function theory and CCSD(T) approaches. Overall the CCSD(T) approach yields the best results. For this property, the B3LYP, BLYP, and BP86 functionals perform better than the BPW91, PBEPBE, and PBE1PBE ones. The accuracy of all the methods is higher if the number of  $3d$  electrons is the same in the neutral atom and the anion. This is especially true for the density functional theory methods.

**Key words:** Density functional theory – CCSD(T) – Electron affinities

## 1 Introduction

Rienstra-Kiracofe et al. [1] recently reviewed the status of density functional theory (DFT) for the treatment of electron affinities (EAs). They demonstrated that, while DFT is not the most accurate approach, it is sufficiently accurate to make useful predictions of EAs and it can be used to study larger molecules than cannot be treated by more accurate techniques. While they did not consider transition-metal-containing species, DFT EA values have been reported [2,3,4,5,6] for several systems containing transition-metal atoms and these computed values agree reasonably well with experiment. These results have been obtained with different basis sets and/or different functionals. Barden et al. showed that DFT does not yield consistently accurate results for the  $w_e$ ,  $r_e$  and  $D_e$  values for transition-metal dimers [7]. That is, some functionals work well for some dimers, but not for others. Thus the question arises, are the recent EA results representative of all transition-metal-containing systems?

Here we compare the EA values of Ti, V, Cr, Fe, Co, Ni, and Cu atoms computed at the DFT level, using several different functionals, with those obtained by the coupled-cluster singles and doubles approach including the effect of connected triples determined using perturbation theory, CCSD(T). Many functionals are currently available and the development of new functionals is an important area of research, especially the question of the self-interaction error [8,9]. However, we restrict ourselves to a few of the commonly used functionals in basis sets that can be applied to sizable molecular systems. We should also note that some highly accurate calculations of transition-metal EAs have been reported [10,11,12], but these approaches would be difficult to apply to molecules, and therefore we restrict ourselves to the CCSD(T) approach, which can be used to calibrate DFT for small molecules. The computed results are compared with experiment [13]. The ground state of  $\text{Sc}^-$  is  $^1D^\circ(3d^14s^24p^1)$  and since this state is not well described by a single reference, we do not include it in our study. Mn has no EA and is, therefore, not included either. Our goal is not to obtain the most accurate atomic EAs possible, but rather to see how the DFT and CCSD(T) approaches perform relative to experiment, and to observe the consistency of the computed results as a function of the metal atom. This should give some insight into the problems that might be faced in the calculation of EAs at the DFT level for systems containing transition-metal atoms. However, it should be remembered that this is only one property and for a different property the functionals could perform very differently, and choice of the optimal functional could be a compromise between the accuracy of many different properties.

## 2 Methods

In the DFT calculations, we consider several different functionals as implemented in Gaussian98 [15]: hybrid [16] B3LYP [17] hybrid PBE1PBE [18], BP86 [19,20], BLYP [19,21], BPW91 [19,22] and PBEPBE [18]. In the DFT calculations, we use the 6-311+G\* basis sets [23,24,25,26]. We impose at least  $D_{2h}$  symmetry in the DFT

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calculations. We achieve this by placing two He atoms at  $\pm 100 \text{ \AA}$  on the  $x$ -axis,  $\pm 90 \text{ \AA}$  on the  $y$ -axis, and  $\pm 95 \text{ \AA}$  on the  $z$ -axis. For many systems we are able to achieve converged solutions with an integral number of  $3d$  electrons; however, for some atoms, there is a mixing of the  $s$  and  $3d$  orbitals when the pure functionals are used. Since the full-configuration-interaction natural orbitals would correspond to solutions with pure orbitals and with nearly integral numbers of  $3d$  electrons, we modified Gaussian94 to prevent mixing of the different types of functions; thus, the BLYP, BP86, and BPW91 results are for solutions that have integral numbers of  $3d$  electrons. Unfortunately we do not have the source code to Gaussian 98 and therefore the PBEPBE results correspond to mixed solutions in a few cases. To put the functionals on equal footing, we do not discuss those cases where the PBEPBE solutions is mixed; however, we do include the results in the tables.

Our highest level of theory is the restricted coupled-cluster singles and doubles approach [27,28], including the effect of connected triples determined using perturbation theory [29,30]. In the valence treatment, we correlate the  $3d$  and  $4s$  electrons. In some calculations of Ti, we also include the metal  $3s$  and  $3p$  electrons in the correlation treatment. The valence basis sets are those optimized by Partridge [31], for Ti, the (21s13p8d) set is used, while for the other atoms, the (20s12p9d) sets are used. To all atoms, we add the three  $p$  and one  $d$  supplemental functions optimized by Partridge. To improve the description of the negative ions, a diffuse  $s$  and a diffuse  $p$  functions are added to each atom. The  $s$  and  $p$  exponents are 0.009 and 0.005 for Ti, 0.010 and 0.007 for V, 0.010 and 0.008 for Cr, 0.011 and 0.009 for Fe, 0.012, and 0.010 for Co, 0.013 and 0.011 for Ni, and 0.013 and 0.012 for Cu. Scalar relativistic effects are included using the Douglas–Kroll–Hess (DKH) approach [32,33]. These primitive basis sets are contracted using nonrelativistic self-consistent-field (SCF) wave functions and using DKH SCF wave functions for the atomic ground state. The first 16  $s$  primitive functions are contracted to three functions and the first ten  $p$  primitives are contracted to two functions, while the remaining primitives are uncontracted. For V–Cu, the first six primitive  $d$  functions are contracted to one function, while for Ti the first five functions are contracted to one function in the valence basis set and the first four functions are contracted to one function in the Ti core–valence basis set. For all the atoms, the averaged atomic natural orbital (6f4g)/[3f2g] polarization sets are used [34].

For SCF and CCSD(T) calculations the occupation that corresponds to the pure ground state is clear [25] and these are the occupations that we used. For hybrid functionals, the same occupations tend to correspond to the lowest-energy solution. However, as discussed by Baerends et al. [14], the occupation that yields the lowest energy for pure functionals can correspond to one that is actually a mixture of ground and excited states. They found that the splitting among the different occupations was up to about 0.3 eV. In this work, we use the same occupation at all levels of theory; thus, the DFT results could change if an occupation that does not correspond to the pure ground state was used. However, as discussed later, our best EA values correspond to the addition of an electron to the  $4s$  orbital, and therefore some of the uncertainty associated with the question of  $3d$  occupation will cancel when the EA is computed since the number of  $3d$  electrons in the neutral atom and the anion are the same.

The CCSD(T) calculations were performed using Molpro [35] which was modified to compute the DKH integrals, while the DFT calculations were performed using the Gaussian 94 or Gaussian 98 programs [15].

### 3 Results and discussion

The ground states of the metal anions studied in this work are derived from the  $3d^{n+1}4s^2$  occupation. The ground state of the neutrals can be derived from either the  $3d^n4s^2$  or  $3d^{n+1}4s^1$  occupations; thus, the EA can correspond to the addition of an electron to either the  $3d$  or  $4s$  the orbitals. The EA value computed with respect

to the neutral ground state is denoted EA(GS). If the neutral ground state has a  $3d^n4s^2$  occupation, we also compute the EA with respect to the  $3d^{n+1}4s^1$  state, which we correct to the ground state using the experimental  $3d^n4s^2 - 3d^{n+1}4s^1$  separations [36]. This alternative approach is denoted EA(4s) since the attachment corresponds to addition of the extra electron to the  $4s$  orbital.

We first consider Cr, Ni, and Cu, which have neutral ground states derived from  $3d^{n+1}4s^1$ ; the results are summarized in Table 1. Using the difference between the CCSD(T) and DKH–CCSD(T) results, we determine the relativistic effect on the EA, and use this difference to determine the nonrelativistic “experimental” value. Since the DFT results do not include scalar relativistic effects, they are compared with this corrected value. Our scalar relativistic correction for Cr is smaller than that found by Osanai et al. [11], but is consistent with the values obtained for the other atoms in this work. We should note that using our relativistic effect instead of their value would reduce the error in their best computed value.

Overall, of the DFT approaches, the hybrid B3LYP approach yields the best agreement with experiment. In fact, on average, the B3LYP results agree slightly better with experiment than the CCSD(T) results. It is interesting that the other hybrid approach considered, PBE1PBE, provides EA values that are consistently smaller than experiment, with an error of 0.34 eV for Cr. The BLYP results agree with experiment to within 0.12 eV and the BP86 values to within 0.22 eV. BPW91 and PBEPBE have fairly sizable errors for Cr, but errors of less than 0.1 eV for Ni and Cu. The error in Cr is especially interesting since there is only one  $3d$  occupation and hence no uncertainty in how best to apply the DFT approach. We should note that the PBEPBE solution for Ni has a  $3d$  population of 8.89 electrons, instead of 9.0.

The results for Ti, V, Fe, and Co are included in Table 2. We first note that the EA(GS) values are in poor agreement with experiment for all of the methods. Even the DKH–CCSD(T) approach has errors ranging

**Table 1.** Summary of computed electron affinity (EA) values for Cr, Ni and Cu. All the values are in electron volts

	EA(GS) <sup>a</sup> Cr	EA(GS) Ni	EA(GS) Cu
BPW91	0.29	1.07	1.16
BLYP	0.61	1.19	1.27
BP86	0.61	1.29	1.37
PBEPBE	0.41	1.15 <sup>b</sup>	1.23
B3LYP	0.65	1.14	1.21
PBE1PBE	0.31	0.91	0.98
CCSD(T)	0.58	1.05	1.09
DKH–CCSD(T)	0.60	1.12	1.17
$\Delta$	0.02	0.07	0.08
Experiment <sup>c</sup>	0.67	1.16	1.23
Nonrelativistic experiment	0.65	1.09	1.15

<sup>a</sup>EA(GS) is computed as the energy difference of the anion and neutral ground states

<sup>b</sup>The neutral state is a mixture of the  $3d^n 4s^2$  and  $3d^{n+1} 4s^1$  occupations

<sup>c</sup>The EA values are from Ref. [13]

from 0.18 to 0.39 eV. An inspection of the  $3d^n 4s^2 - 3d^{n+1} 4s^1$  separations shows that it is hard to describe states with different numbers of  $d$  electrons. We should note that the CCSD(T) results have smaller errors than the DKH-CCSD(T) values since the relativistic effects actually increase the error in the  $3d^n 4s^2 - 3d^{n+1} 4s^1$  separations. The EA(4s) approach avoids the error associated with states with different numbers of  $3d$  electrons by computing the energy associated with adding an electron to the  $4s$  orbital, and uses experimental data to correct the computed value to a ground-state EA result. Since this approach reduces the error in the CCSD(T) and DKH-CCSD(T) values, we use EA(4s) values to compute our relativistic correction.

The EA(4s) approach reduces the maximum error in the DKH-CCSD(T) approach to 0.12 eV, which is similar to that found for Cr, Ni, and Cu. For Ti, correlating the  $3s$  and  $3p$  semicore electrons reduces the error in the  $3d^n 4s^2 - 3d^{n+1} 4s^1$  separation and improves the EA(GS) value, but the EA(4s) value is hardly affected by core correlation, since most of the differential  $3s3p$  effect is associated with states possessing different numbers of  $3d$  electrons.

For the DFT approaches, the EA(4s) values are better than the EA(GS) values, but the errors can still be sizable. The B3LYP results have an average absolute

error of 0.078 eV and a maximum error of 0.16 eV (for Ti), which is larger than found for Cr, Ni, and Cu, but quite similar to the DKH-CCSD(T) approach. The BP86 approach has an average absolute error of 0.088 eV and is the second-best approach, while the BLYP is third best, with an average absolute error 0.10 eV. Thus, the B3LYP, BP86, and BLYP approaches have similar errors for all of the metal atoms studied. The PBE1PBE EA(4s) results are consistently smaller than the experimental values, as found for Cr, Ni, and Cu. The BPW91 results are also too small, but the errors are smaller than those found for PBE1PBE. Excluding Ni and Fe, the PBEPBE EA (4s) results are not affected by mixing of the  $3d^n 4s^2$  and  $3d^{n+1} 4s^1$  occupations, but even in the cases where mixing is not a problem, this functional yields EA values that tend to be too small. Like the BPW91 approach, the errors tend to be larger for the early metals than for the late metals.

## 4 Conclusions

Overall the three best functionals for the calculation of the atomic EA values are B3LYP, BP86, and BLYP, provided that the number of  $3d$  electrons does not change between the neutral atom and the anion. The

**Table 2.** Summary of computed EA values and the separation,  $\Delta_{sd}$ , between the neutral states derived from the  $3d^n 4s^2$  and  $3d^{n+1} 4s^1$  occupations. All the values are in electron volts

	EA(GS) <sup>a</sup>	EA(4s) Ti	$\Delta_{sd}$	EA(GS)	EA(4s) V	$\Delta_{sd}$	
BPW91	0.86	-0.38	-0.42	1.34	0.11	-0.98	
BLYP	0.60	-0.15	0.06	1.01	0.39	-0.38	
BP86	0.94	-0.08	-0.21	1.41	0.42	-0.74	
PBEPBE	0.83	-0.26	-0.27	1.11 <sup>b</sup>	0.24	-0.62 <sup>b</sup>	
B3LYP	0.48	-0.11	0.22	0.87	0.43	-0.19	
PBE1PBE	0.49	-0.36	-0.05	0.95	0.13	-0.57	
CCSD(T)val	-0.17	-0.05	0.93	0.37	0.43	0.93	
CCSD(T)3s3p	0.01	-0.07	0.73				
DKH-CCSD(T)val	-0.28	-0.02	1.07	0.23	0.45	0.47	
DKH-CCSD(T)3s3p	-0.10	-0.04	0.88				
$\Delta_{val}$	-0.11	0.03	0.14	-0.15	0.02	-0.45	
$\Delta_{3s3p}$	-0.12	0.03	0.15				
Experimental	0.08	0.08	0.81	0.53	0.53	0.25	
Nonrelativistic experiment		0.05			0.51		
		Fe			Co		
BPW91	1.13	-0.13	-0.39	1.61	0.49	-0.70	
BLYP	1.08	0.06	-0.15	1.53	0.64	-0.47	
BP86	1.31	0.12	-0.32	1.77	0.72	-0.64	
PBEPBE	0.69 <sup>b</sup>	-0.18 <sup>b</sup>	0.00 <sup>b</sup>	1.61	0.59	-0.59	
B3LYP	0.71	0.05	0.21	1.15	0.61	-0.12	
PBE1PBE	0.45	-0.19	0.22	0.92	0.38	-0.12	
CCSD(T)	-0.05	-0.01	0.91	0.59	0.54	0.37	
DKH-CCSD(T)	-0.25	0.04	1.16	0.35	0.60	0.67	
$\Delta$	-0.21	0.05	0.25	-0.24	0.06	0.30	
Experiment	0.16	0.16	0.87	0.66	0.66	0.42	
Nonrelativistic experiment		0.11			0.60		

<sup>a</sup> EA(GS) is computed as the energy difference of the anion and neutral ground states, while EA(4s) is computed as the energy difference between the ground state of the anion and the lowest neutral state with a  $3d^{n+1} 4s^1$  occupation, which is corrected to the neutral ground state using the experimental separation between the lowest states arising from the  $3d^n 4s^2$  and  $3d^{n+1} 4s^1$  occupations

<sup>b</sup> The neutral state is a mixture of the  $3d^n 4s^2$  and  $3d^{n+1} 4s^1$  occupations

<sup>c</sup> The EA values are from Ref. [13] and the  $\Delta_{sd}$  values are from Ref. [36]

largest error for these three functionals is about twice that found for the CCSD(T) approach. The errors for the other three functionals are significantly larger for some of the atoms studied. It would be interesting to study the same functionals using the same basis sets for some molecular EAs to see if the atomic errors carry over to the molecular systems as found for systems composed of atoms from the first two rows of the periodic table [1]. While small errors in the atomic EAs do not guarantee small errors in molecular values, the results presented here suggest that molecular EAs that correspond to a change in the number of  $3d$  electrons can have much larger errors than those that correspond to adding an electron to an  $s$  (or presumably a  $p$ ) orbital.

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## References

- Rienstra-Kiracofe JC, Tschumper GS, Schaefer HF, Nandi S, Ellison GB (2002) *Chem Rev* 102: 231
- Gonzales JM, King RA, Schaefer HF (2000) *J Chem Phys* 113: 567
- Walch MB, King KR, Schaefer HF (1999) *J Chem Phys* 110: 5224
- Vybioshchikov SF, Sauer J (2000) *J Phys Chem A* 104: 10913
- Gutsev GL, Jena P, Zhai H-J, Wang L-S (2001) *J Chem Phys* 115: 7935
- Gutsev GL, Khanna SN, Rao BK, Jena P (1999) *J Phys Chem A* 103: 5812
- Barden CJ, Rienstra-Kiracofe JC, Schaefer HF (2000) *J Chem Phys* 113: 690
- Perdew JP, Zunger A (1981) *Phys Rev* 23: 5048
- Chen J, Kreiger JB, Li Y, Iafrate GJ (1996) *Phys Rev A* 54: 3939
- Mitas L (1994) *Phys Rev A* 49: 4411
- Osanai Y, Isikawa H, Miura N, Noro T (2001) *Theor Chem Acc* 105: 437
- Dzuba VA, Flambaum VV, Gribakin GF, Harabati C (1999) *Phys Rev A* 60: 3641
- Hotop H, Lineberger WC (1985) *J Phys Chem Ref Data* 14: 731
- Baerends EJ, Branchadell V, Sodupe M (1997) *Chem Phys Lett* 265: 481
- Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Zakrzewski VG, Montgomery JA Jr, Stratmann RE, Burant JC, Dapprich S, Millam JM, Daniels AD, Kudin KN, Strain MC, Farkas O, Tomasi J, Barone V, Cossi M, Cammi R, Mennucci B, Pomelli C, Adamo C, Clifford S, Ochterski J, Petersson GA, Ayala PY, Cui Q, Morokuma K, Salvador P, Dannenberg JJ, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Cioslowski J, Ortiz JV, Baboul AG, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Gomperts R, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PMW, Johnson B, Chen W, Wong MW, Andres JL, Gonzalez C, Head-Gordon M, Replogle ES, Pople JA (2001) *Gaussian 98*, revision All. Gaussian Pittsburgh PA
- Becke AD (1993) *J Chem Phys* 98: 5648
- Stephens PJ, Devlin FJ, Chabalowski CF, Frisch MJ (1994) *J Phys Chem* 98: 11623
- (a) Perdew JP, Burke K, Ernzerhof M (1996) *Phys Rev Lett* 77: 3865; (b) Erratum (1997) *Phys Rev Lett* 78: 1396
- Becke AD (1988) *Phys Rev A* 38: 3098
- (a) Perdew JP (1986) *Phys Rev B* 33: 8822; (b) Erratum (1986) *Phys Rev B* 34: 7406
- Lee C, Yang W, Parr RG (1988) *Phys Rev B* 37: 785
- Perdew JP, Wang Y (1991) *Phys Rev B* 45: 13244
- Frisch MJ, Pople JA, Binkley JS (1984) *J Chem Phys* 80: 3265, and references therein
- Wachters AJH (1970) *J Chem Phys* 52: 1033
- Hay PJ (1977) *J Chem Phys* 66: 4377
- Raghavachari K, Trucks GW (1989) *J Chem Phys* 91: 1062
- Bartlett RJ (1981) *Annu Rev Phys Chem* 32: 359
- Knowles PJ, Hampel C, Werner H-J (1993) *J Chem Phys* 99: 5219
- Raghavachari K, Trucks GW, Pople JA, Head-Gordon M (1989) *Chem Phys Lett* 157: 479
- Watts JD, Gauss J, Bartlett RJ (1993) *J Chem Phys* 98: 8718
- Partridge H (1989) *J Chem Phys* 90: 1043
- Douglas M, Kroll NM (1974) *Ann Phys NY* 82: 89
- Hess BA (1986) *Phys Rev A* 33: 3742
- Bauschlicher CW (1995) *Theor Chim Acta* 92: 183
- Werner H-J, Knowles PJ *MOLPRO* (a package of ab initio programs) with contributions from Almlöf J, Amos RD, Berning A, Cooper DL, Deegan MJO, Dobbyn AJ, Eckert F, Elbert ST, Hampel C, Lindh R, Llyod AW, Meyer W, Nicklass A, Peterson K, Pitzer R, Stone AJ, Taylor PR, Mura ME, Pulay P, Schütz M, Stoll H, Thorseinsson T
- Moore CE (1949) *Atomic energy levels. Natl Bur Stand US circ* 467