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BFW: A Density Functional for Transition Metal Clusters

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Ionization potentials (IPs) or electron affinities (EAs) for transition metal clusters are an important property that can be used to identify and differentiate between clusters. Accurate calculation of these values is therefore vital. Previous attempts using a variety of DFT models have correctly predicted trends, but have relied on the use of scaling factors to compare to experimental IPs. In this paper, we introduce a new density functional (BFW) that is explicitly designed to yield accurate, absolute IPs for transition metal clusters. This paper presents the numerical results for a selection of transition metal clusters and their carbides, nitrides, and oxides for which experimental IPs are known. When tested on transition metal clusters, the BFW functional is found to be significantly more accurate than B3LYP and B3PW91.

1. Introduction

The past decade has seen an explosion in the experimental and theoretical study of transition metal clusters.[1−11] Due to the size-dependent variation of each cluster's electronic and geometric structure, the interaction of a molecule with a specific cluster is unique, yielding species with novel chemical and physical properties.[5−7] Consequently, considerable effort has gone into understanding the physical and chemical properties of molecules, both experimentally and computationally. However, the partially filled *d*-shells of the metal atoms that constitute the clusters make this a difficult task.

For transition metal clusters, two of the most readily determined physical properties are the ionization potential (IP) or electron affinity (EA). These are easily obtained experimentally over a large range of sizes and their importance in understanding cluster properties has been documented in several reviews.[1−5,7] It has been shown that the IP and EA can provide information about electronic and geometric structure as well as chemical reactivity with other molecules. Therefore, the ability to accurately calculate IPs and EAs, and compare them with experiment, can provide an important component to understanding the physical and chemical properties of metal clusters. The reaction between Ag clusters and ethylene is an example where the use of IP information has been instrumental in determining the structure. For $Ag_3-C_2H_4$, DFT calculations predict two close-lying minima where the μ-bonded ethylene is either μ_1 or μ_2 bonded. Relative to Ag_3, the two isomers were predicted to have lower and higher IPs, respectively, the former being in better agreement with experiment.[5,11] More recent work by some of the present authors has shown that the reaction of CO with Nb_3 and Nb_4 yields a product with an IP that is consistent with DFT calculations in which the CO is dissociated.[12]

Hence, it is important to have the best possible computational tool for calculating absolute IPs and EAs for transition metal clusters and the relative changes that occur upon binding to a variety of molecules. However, accurately calculating these values has been shown to be problematic.[13] Due to the large number of electronic states that must be considered, ab initio methods require multiconfigurational approaches and calculations are largely intractable for all but the very smallest clusters. Present DFT methods give values that vary dramatically with the chosen functional and basis set, which is not surprising since metal cluster species are not included in their parametrization. Therefore, by optimizing a specific functional for cluster species, it may be possible to improve the performance of DFT for calculating such parameters.

In this paper we present a simple DFT functional for calculating IPs and EAs of transition metal clusters (and their carbides, nitrides and oxides). Following the procedure used to optimize the EDF1[22] and EDF2[23] functionals, we have developed a density functional specifically for IPs and EAs of metal clusters. The training set consists of 47 metal atoms and metal-containing diatomic molecules. We apply our functional to a set of larger metal clusters and find that it yields results that are significantly improved over those of the popular B3LYP and B3PW91 functionals.

2. Method

A common strategy in forming new density functionals, is the recombination of existing functionals into a compound functional. B3LYP,[14] one of the most successful and widely used functionals, is of this form and comprises exact (or Fock[15]) exchange, the Dirac[17] and Becke'88[16] exchange functionals, and the Vosko−Wilk−Nusair[18] and Lee−Yang−Parr[19] correlation functionals. Other functionals of this form include the family of empirical density functionals; EDF1 and EDF2.

The determination of the linear mixing coefficients in these functionals is usually achieved by minimizing the residual error between the predicted and experimentally measured values for a set of training data. This results in a functional that depends not only on the choice of component functionals, but also on the choice of training data. In practice this choice of data is dictated by the availability of accurately determined experi-

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TABLE 1: The 26 Transition Metal Atoms in the Training Set[a]

	neutral state	cation state	expt	exp-BFW	exp-B3LYP	exp-B3PW91
Sc	$^{2}D_{3/2}$	$^{3}D_{1}$	6.56	0.00	0.03	0.15
Ti	$^{3}F_{2}$	$^{4}F_{3/2}$	6.83	0.24	0.24	0.50
V	$^{4}F_{3/2}$	$^{5}D_{0}$	6.75	−0.13	0.04	0.01
Mn	$^{3}F_{2}$	$^{7}S_{3}$	7.43	−0.15	−0.12	0.21
Fe	$^{6}S_{5/2}$	$^{6}D_{9/2}$	7.90	−0.15	−0.13	0.11
Co	$^{4}F_{9/2}$	$^{3}F_{4}$	7.88	0.34	0.07	0.10
Ni	$^{3}F_{4}$	$^{2}D_{5/2}$	7.64	−0.03	−0.3	−0.25
Cu	$^{2}S_{1/2}$	$^{1}S_{0}$	7.73	−0.18	−0.45	−0.38
Zn	$^{1}S_{0}$	$^{2}S_{1/2}$	9.39	−0.09	−0.13	0.00
Y	$^{2}D_{3/2}$	$^{1}S_{0}$	6.22	−0.11	−0.12	−0.29
Zr	$^{3}F_{2}$	$^{4}F_{3/2}$	6.63	0.06	0.06	0.26
Nb	$^{6}D_{1/2}$	$^{5}D_{0}$	6.76	0.00	−0.17	−0.33
Mo	$^{7}S_{3}$	$^{6}S_{5/2}$	7.09	0.02	−0.14	−0.33
Tc	$^{6}S_{5/2}$	$^{7}S_{3}$	7.28	0.05	−0.16	−0.28
Ru	$^{5}F_{5}$	$^{4}F_{9/2}$	7.36	−0.01	−0.25	−0.32
Rh	$^{4}F_{9/2}$	$^{3}F_{4}$	7.46	0.02	−0.24	−0.27
Pd	$^{1}S_{0}$	$^{2}D_{5/2}$	8.34	−0.17	−0.26	−0.28
Ag	$^{2}S_{1/2}$	$^{1}S_{0}$	7.58	−0.06	−0.31	−0.27
Cd	$^{1}S_{0}$	$^{2}S_{1/2}$	8.99	0.05	−0.04	0.07
Ta	$^{4}F_{3/2}$	$^{5}F_{1}$	7.89	−0.07	0.31	0.59
W	$^{5}D_{0}$	$^{6}D_{1/2}$	7.98	0.12	0.25	0.48
Re	$^{6}S_{5/2}$	$^{7}S_{3}$	7.88	0.02	0.07	0.48
Os	$^{5}D_{4}$	$^{7}D_{9/2}$	8.70	0.02	0.30	0.55
Ir	$^{4}F_{9/2}$	$^{5}F_{5}$	9.10	−0.13	0.14	0.11
Pt	$^{3}D_{3}$	$^{2}D_{5/2}$	9.00	0.02	−0.16	−0.19
Au	$^{2}S_{1/2}$	$^{1}S_{0}$	9.23	0.23	−0.01	−0.01
MAD (atoms)				**0.10**	**0.17**	**0.26**
MSD (atoms)				**0.00**	**−0.06**	**0.02**

[a] The Cr, La, Hf, and Hg atoms were excluded because of either SCF convergence difficulties or lack of available ECPs for the SRSC basis set. Atomic data were obtained from the NIST database.[20] Calculated differences (eV) for the functionals tested are shown in the final three columns.

mental values, such as those in the G2 data set.[24] For transition-metal clusters, few reliable thermochemical data are available in the literature and for this reason we were limited to transition-metal atoms, metal−metal dimers and metal oxides for which the ionization potentials (IPs) or electron affinities (EAs) are well-established. Systems larger than diatomics were ruled out due to difficulties in obtaining reliable experimental values and/or uncertainties in the electronic states involved. A list of the 47 systems in the training set is shown in Tables 1 and 2.

For each system in the training set a reference density was computed using the B3LYP functional and SRSC effective core potential and associated basis set.[25,26] Bond lengths for diatomics were optimized at the same level of theory and are listed in Table 2. Five exchange functionals (Fock[15] Dirac,[17] Becke'88,[16] Perdew−Wang '91[30] and Gill '96[32]) and six correlation functionals (Perdew '86,[27] Perdew−Zunger,[28] Vosko−Wilk−Nusair fifth parametrization,[18] Lee−Yang−Parr,[19] Wigner[29] and Perdew−Wang '91[30]) were applied to these reference densities to obtain a set of 11 non-self-consistent energy vectors. Corrections for differences in zero-point vibrational energies are small in the reactions considered, and were not included. All calculations were undertaken using a development version of the QChem 3.0[31] software package using a 50 point Euler−Maclaurin radial grid and 302 point Lebedev grid for angular integration.

Estimates of the mixing coefficients were obtained by performing 'external' optimizations[22] using the non-self-consistent energies. This involved considering all possible k-subsets of the 11 energy vectors for $1 \leq k \leq 10$ and performing a linear regression using each subset of functionals to determine the optimal values of the mixing coefficients. No constraints were imposed on the coefficients and for simplicity, we included exchange-only and correlation-only combinations. This gives rise to a total of 2046 different functionals which, for each value of k, were ranked according to their mean absolute deviation (MAD).

As k increases from $1 \rightarrow 3$, the MAD of the optimal combination of functionals decreases sharply from 0.45 to 0.23 to 0.16 eV. This is to be expected as the increased flexibility of the functional is better able to model the data. The MAD decreases slightly to 0.158 eV for $k = 4$, but beyond this it remains almost constant and does not drop below 0.153 eV. The absence of significant improvement beyond $k = 3$ indicates that there are appreciable linear dependencies within our functional basis. This, too, is to be expected as each exchange (correlation) functional is trying to model the same component of the total energy. On the basis of these results, it was decided to restrict our attention to three-parameter functionals. A list of the top five three-parameter functionals is shown in Table 3.

The five functionals shown in Table 3 can be divided into two distinct classes: The first are those based on the Wigner correlation functional, include around 29% exact exchange and have exchange coefficients that sum to 1.02. The second are those functional combinations based on the PW91 correlation functional. Both of these include 37% exact exchange and have exchange coefficients that sum to only 0.92. This, along with the much larger coefficient of the correlation component in these functionals, indicates there is a significant portion of the exchange energy that is being captured by the PW91 correlation functional.

It is clear that the Wigner-based functionals perform better for this set of training data, however, there is little to choose between them. We selected the first combination, (B88, HF and Wigner) and used this as a basis for further refinement. A 5 × 5 × 5 grid, centered at the coefficients in Table 3 was constructed, with step sizes corresponding to 5% of each coefficient. The *self-consistent* energies for all the members of the training set, along with the associated MAD values were computed at each of these grid points. Of these 125 self-consistent MAD values, the lowest (0.154 eV) was obtained by decreasing the Wigner coefficient by 5%, while leaving the B88 and HF coefficients unchanged. We attempted to further minimize this error by fitting a tri-quartic polynomial to the grid points values and finding the minimum on this three-dimensional surface, however, when the new estimates of the mixing parameters where used self-consistently, there was no improvement over the best grid point value.

The final form of our proposed functional is based on the best grid value and is given by

$$E_{\mathrm{XC}} = 0.736E_{\mathrm{X}}^{\mathrm{B88}} + 0.286E_{\mathrm{X}}^{\mathrm{Fock}} + 1.178E_{\mathrm{C}}^{\mathrm{Wigner}} \qquad (1)$$

We call this the BFW functional and it can be considered as a hybridized form of the Becke−Wigner functional that was proposed some time ago.[33]

3. Results and Discussion

Tables 1 and 2 contain the results of applying the BFW, B3LYP and B3PW91 functionals to the training set, B3PW91 was included as it has recently been successfully applied to clusters by Fielicke and co-workers.[34] Geometries for the diatomics were fixed at the B3LYP values to allow consistent comparison. As a test, geometry optimizations were also performed with each of the three functionals and it was found that the IPs changed very little. For the 26 transition metal atoms in the set BFW has a MAD of 0.10 eV, compared with 0.17

TABLE 2: The 21 Dimeric Species in the Training Set[a]

	neutral state	B3LYP bondlength ([angst]A)	cation state	B3LYP bondlength (Å)	exp.	exp-BFW	exp-B3LYP	exp-B3PW91
V_2	$^3\Sigma^-$	2.00	$^4\Sigma^-$	1.86	6.36	0.10	0.04	−0.05
Cr_2	$^1\Sigma_g{}^+$	1.60	$^2\Sigma_g{}^+$	1.58	7.00	−0.06	−0.50	−0.49
Cu_2	$^1\Sigma_g{}^+$	2.25	$^1\Sigma_g{}^-$	2.39	7.90	−0.02	−0.23	−0.14
Nb_2	$^3\Sigma^-$	2.07	$^4\Sigma^-$	2.02	6.37	0.05	0.01	0.02
Mo_2	$^1\Sigma_g{}^+$	1.96	$^2\Sigma_g{}^+$	1.94	6.95	0.07	−0.05	−0.07
Ag_2	$^1\Sigma_u{}^+$	2.61	$^2\Sigma_g{}^-$	2.76	7.66	0.12	−0.12	−0.07
TiO	$^3\Delta$	1.63	$^2\Delta_{3/2}$	1.59	6.82	−0.24	−0.38	−0.37
VO	$^4\Sigma^-$	1.64	$^3\Sigma^-$	1.61	7.25	0.44	0.44	0.45
CrO	$^5\Pi$	1.65	$^4\Sigma^-$	1.65	7.85	−0.52	0.90	0.93
FeO	$^5\Delta_4$	1.65	$^6\Sigma$	1.68	8.56	0.13	0.07	0.18
CuO	$^2\Pi_{3/2}$	1.77	$^3\Sigma$	1.84	9.41	−0.01	−0.07	0.32
ZrO	$^3\Delta$	1.77	$^2\Sigma^-$	1.73	6.81	0.00	−0.15	−0.17
MoO	$^5\Pi$	1.74	$^4\Sigma^-$	1.68	7.45	−0.30	0.85	0.80
NbO	$^4\Sigma^-$	1.76	$^3\Sigma^-$	1.69	7.15	−0.12	−0.26	−0.35
TaO	$^2\Delta$	1.77	$^1\Sigma$	1.71	8.61	0.46	0.48	0.28
NiO^-	$^2\Pi_{3/2}$	1.68	$^3\Sigma^-$	1.65	1.47	0.09	0.18	0.16
PdO^-	$^2\Pi_{3/2}$	1.86	$^3\Sigma^-$	1.90	1.67	0.54	0.46	0.44
PtO^-	$^2\Pi_{3/2}$	1.83	$^3\Sigma^-$	1.90	2.17	−0.08	−0.02	−0.10
RhC^-	$^3\Pi$	1.69	$^2\Sigma^+$	1.65	1.46	0.93	0.87	0.80
RhN^-	$^2\Pi$	1.77	$^1\Sigma^+$	1.66	1.58	0.20	0.16	0.18
RhO^-	$^3\Sigma^-$	1.81	$^4\Sigma_{3/2}$	1.76	1.51	−0.23	−0.27	−0.28
MAD (dimers)						**0.21**	**0.32**	**0.32**
MSD (dimers)						**0.07**	**0.11**	**0.12**
MAD (overall)						**0.15**	**0.24**	**0.29**
MSD (overall)						**0.03**	**0.02**	**0.06**

[a] Data for dimers were obtained through DiRef[21] and references therein. Calculated differences (eV) for the functionals tested are shown in the final three columns.

TABLE 3: The Five Combinations of Functionals with the Lowest MAD[a]

MAD (eV)	functionals in the mix
0.162	$0.286E_X^{Fock} + 0.736E_X^{B88} + 1.240E_C^{Wigner}$
0.164	$0.295E_X^{Fock} + 0.728E_X^{PW91} + 1.132E_C^{Wigner}$
0.164	$0.284E_X^{Fock} + 0.733E_X^{Gill96} + 1.389E_C^{Wigner}$
0.171	$0.373E_X^{Fock} + 0.551E_X^{PW91} + 1.698E_C^{PW91}$
0.173	$0.373E_X^{Fock} + 0.544E_X^{B88} + 1.818E_C^{PW91}$
0.214	B3LYP

[a] Note that these are based on the non-self-consistent energies obtained from B3LYP/SRSC densities. The (self-consistent) B3LYP MAD is also shown for comparison.

TABLE 4: MAD and MSD Errors (eV) for the IPs of Transition Metal Complexes

	expt	exp-BFW	exp-B3LYP	exp-B3PW91
Y_2	4.98	0.11	−0.07	−0.11
Y_3	5.00	0.16	−0.04	−0.14
Y_3C_2	4.22	0.10	−0.13	−0.15
Zr_3	5.22	0.20	0.09	−0.03
Zr_3O	5.19	0.17	0.00	−0.01
Nb_3	5.80	0.07	−0.18	−0.25
Nb_3C_2	5.05	0.07	−0.09	−0.08
Nb_3O	5.51	−0.05	−0.20	0.25
Nb_3CO	5.82	−0.02	−0.21	−0.23
$Nb_3(CO)_2$	5.85	−0.14	−0.26	−0.26
Nb_3N_2	5.44	−0.09	−0.25	−0.27
MAD		**0.11**	**0.14**	**0.16**
MSD		**0.05**	**−0.12**	**−0.16**

and 0.26 eV for B3LYP and B3PW91, respectively. Upon inclusion of the diatomic species, these values increase to 0.15, 0.24, and 0.29 eV, respectively, as shown at the bottom of Table 2. Similarly, the mean signed deviation (MSD) of the BFW functional are improved over B3LYP and B3PW91 for the atomic and diatomic sets. Fortuitous cancellation of errors results in the overall MSD for B3LYP being slightly better than that of BFW. Overall, it is clear that BFW significantly out-performs the other two functionals for this training set.

In order to test the performance of the new functional on metal clusters, we needed to use only species whose geometric and electronic structure have been unambiguously characterized; these are listed in Table 4. Most of these species have been characterized by PFI-ZEKE, which is capable of extremely accurate ionization potential determinations (±3 cm^{-1}). Moreover, geometric information is conveyed in the vibronic features of the spectrum, although they rely on comparisons with predicted geometric structures. Yang and Hackett[35] have performed such experiments on a range of metal clusters and some of their carbides, nitrides and oxides. Other species for which ZEKE spectra are available have not been included, i.e., V_3, V_4, Nb_5, and Nb_5X ($X = C_2, N_2$). For these species there is considerable uncertainty about their structures since insufficient vibronic information is carried in their spectra. However, we have included the species Nb_3, Nb_3CO and $Nb_3(CO)_2$. These species have only had their IPs determined by photoionization efficiency (with an error of 0.05 eV), however, we have included them due to their similarity to the other niobium cluster species.[12] Clusters containing late transition metal atoms generally have much higher ionization potentials that make them more difficult to characterize experimentally and therefore were not selected for the test set.

Published DFT geometries were used as the starting guesses for B3LYP optimizations. Single point energies using the new BFW functional as well as B3PW91 were carried out on the optimized structures. The maximum overlap method[38] was employed in the single point energy calculations to ensure that the correct electronic state was maintained. The results are shown in Table 4.

Overall, the predicted ionization potentials for the BFW functional are better than B3LYP and B3PW91, as can be seen in Table 4. The mean signed deviations of BFW, B3LYP and B3PW91 are +0.05, −0.12, and −0.12 eV, respectively, showing that, unlike B3LYP and B3PW91, the new functional tends to underestimate IPs. The MAD value for the BFW functional is also less than those of the others, indicating that

TABLE 5: Experimental[35] and Calculated Frequencies (cm^{-1}) for Clusters in the Test Set.

		expt	BFW	B3LYP	B3PW91
Y_2	ν_s(M−M)	185	185	188	192
Y_2^+	ν_s(M−M)	197	213	213	216
Y_3C_2	$\delta(M_n)$	82	82	96	107
$Y_3C_2^+$	$\delta(M_n)$	86	98	108	99
$Y_3C_2^+$	ν_s(M−M)	228	239	239	244
Zr_3	$\delta(M_n)$	177	197	203	185
Zr_3	ν_s(M−M)	258	279	284	287
Zr_3O^+	ν_s(M−M)	272	276	277	262
Nb_3	$\delta(M_n)$	227	218	226	245
Nb_3	ν_s(M−M)	335	367	361	370
Nb_3C_2	$\delta(M_n)$	237	233	249	263
Nb_3C_2	ν_s(M−M)	327	353	357	368
$Nb_3C_2^+$	$\delta(M_n)$	258	265	265	272
$Nb_3C_2^+$	ν_s(M−M)	339	352	360	370
$Nb_3N_2^+$	$\delta(M_n)$	257	324	377	386
Nb_3O	$\delta(M_n)$	330	332	346	350
Nb_3O	ν_s(M−L)	720	709	704	715
Nb_3O^+	$\delta(M_n)$	312	304	308	316
MAD			**15**	**27**	**31**
MSD			**11**	**25**	**29**

TABLE 6: RMS Thermochemical Errors (kcal/mol) for Functionals

rms errors (kcal/mol)	exp-BFW	exp-B3LYP	exp-B3PW91
atomization energies	13.48	8.10	6.10
ionization potentials	8.62	5.05	6.63
electron affinities	6.53	4.40	5.16
proton affinities	7.33	5.51	5.80

its error distribution is narrower and suggesting that BFW is likely to reproduce IP trends more reliably than B3LYP and B3PW91.

BFW underestimates the IPs of the pure metal clusters (Y_2, Y_3, Zr_3, and Nb_3) by 0.07−0.20 eV. The B3PW91 functional overestimates these values by 0.03−0.25 eV. B3LYP overestimates all species except Zr_3. For the doped-clusters, BFW clearly performs better however this is to be expected given the bias toward metal−second row dimers in the training set. The exception to this is Zr_3O, for which B3LYP and B3PW91 fortuitously calculate the value almost exactly.

Vibrational information is also known for all of the species in Table 5 (for both neutral and cation) through their ZEKE spectra (Nb_3 and Zr_3 data were obtained through matrix isolation Raman experiments).[36,37] It was decided to test the ability of the new functional with respect to vibrational frequencies. In order to do this it was necessary to optimize the geometries of each cluster species (which has negligible effects on the IPs calculated above) and their harmonic vibrational frequencies were subsequently calculated. B3LYP geometries were used as the starting guesses for BFW and B3PW91 optimizations and the results are shown in Table 5 along with the experimental frequencies. The BFW frequencies are significantly improved over B3LYP and B3PW91, with MAD values of 15, 27, and 31 cm^{-1} respectively. In particular, low-frequency symmetric bending modes ($\delta(M_n)$) are accurately calculated. The only poor result for BFW is for the Nb_3N_2 singlet cation, although it is better than the B3LYP and B3PW91 frequencies.

Out of curiosity, the new BFW functional was applied to the thermochemical values contained in the well-known G2 data set. In combination with the 6-31+G* basis set, atomization energies, IPs, EAs and proton affinities were calculated and the results are summarized in Table 6. While this performance is mediocre, it is acceptable given that a functional tailored for a particular purpose often struggles when applied well outside its region of strength.

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