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TiCl, TiH, and TiH^+ bond energies: a test of a correlation-consistent Ti basis set

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Abstract. Correlation-consistent basis sets are developed for the Ti atom. The polarization functions are optimized for the average of the ^3F and ^5F states. One series of correlation-consistent basis sets is for 3*d* and 4*s* correlation, while the second series includes 3*s* and 3*p* correlation as well as 3*d* and 4*s* correlation. These basis sets are tested using the Ti ^3F–^5F separation and the dissociation energies of TiCl $X^4\Phi$, TiH $X^4\Phi$, and TiH^+ $X^3\Phi$. The CCSD(T) complete basis set limit values are determined by extrapolation. The Douglas–Kroll approach is used to compute the scalar relativistic effect. Spin-orbit effects are taken from experiment and/or are computed at the CASSCF level. The Ti ^3F–^5F separation is in excellent agreement with experiment, while the TiCl, TiH, and TiH^+ bond energies are in good agreement with experiment. Extrapolation with the valence basis set is consistent with other atoms, while including 3*s* and 3*p* correlation appears to make extrapolation more difficult.

Key words: Basis Set – Bond energies – Correlation-consistent – Inner-shell correlation

1 Introduction

Extrapolation of results obtained using the coupled-cluster singles and doubles approach [1], including the effect of connected triples determined using perturbation theory [2], CCSD(T), in conjunction with correlation-consistent basis sets [3], has resulted in many highly accurate bond energies. Many applications require accurate bond energies for transition-metal-containing systems, and therefore it is highly desirable to extend such systematic basis sets to the transition-metal atoms. However, transition metals are a real challenge for theory, because there are low-lying atomic states that are difficult to describe, but which can contribute to the bonding. Also, 3*s* and 3*p* inner-shell-correlation, spin-orbit, and scalar relativistic effects may be important, and there is a lack of accurate experimental data for comparison. In this paper correlation-consistent basis sets for Ti are developed and tested for the ^3F–^5F separation in Ti and for the bond energies of TiCl, TiH, and TiH^+.

2 Methods

Most calculations are performed using the restricted CCSD(T) approach [4, 5]. The triple-zeta (TZ), quadruple-zeta (QZ), and quintuple-zeta (5Z) augmented-correlation-consistent polarized-valence (aug-cc-pV) sets [3, 6, 7] are used for Cl and the cc-pV sets are used for H. The Ti sets are described below. To improve the accuracy of the CCSD(T) results, we extrapolate to the complete-basis-set (CBS) limit using the three-point ($n^{-4} + n^{-6}$) and variable $\alpha(n^{-\alpha})$ schemes described by Martin [8]. We also discuss the results obtained using the n^{-3} and n^{-4} two-point schemes [8, 9].

The scalar relativistic effects are computed using the one-electron Douglas–Kroll (DK) approximation [10]. Two separate modified coupled-pair functional (MCPF) calculations [11] are performed: one with the nonrelativistic Hamiltonian and one with the DK Hamiltonian. These calculations are performed using the TZ basis set, but with two different contractions. The nonrelativistic contraction coefficients are taken from the nonrelativistic self-consistent-field (SCF) orbitals, while the DK contraction coefficients are taken from the DK SCF orbitals. The scalar relativistic effect is taken as the difference between these two MCPF calculations.

The spin-orbit effect is taken from experiment [12] or is computed at the full-valence complete-active-space SCF (CASSCF) level. For the spin-orbit calculations, the Ti basis set is taken from Wachters [13] and has a diffuse d function added [14], while the 6-311+G* set [15] is used for Cl and the cc-pV double-zeta set is used for H. The smaller basis sets are used for the spin-orbit calculations because of restrictions in the current spin-orbital integral program, for example, only segmented basis sets can be used.

The CCSD(T) and CASSCF calculations performed using Molpro [16, 17], while the MCPF calculations are performed using Molecule-Sweden [18]. The closed-shell CCSD program is described in Ref. [17]. The DK integrals are computed using a modified version of the program written by Hess [10].

3 Ti basis set

The bonding in transition-metal compounds is known to involve mixtures of the low-lying occupations [19]. For Ti this includes the $^3F(3d^24s^2)$ and $^5F(3d^34s^1)$ states. Since the 4*s* orbital is much more diffuse than the 3*d* orbital, the two states have very different correlation energies, and therefore it is difficult to treat these two states equivalently. The different number of *s* electrons also means that the two states have different relativistic energies, since relativity mostly affects *s* electrons. An optimization of the polarization functions for either state is expected to introduce a bias into the basis set, and therefore we performed separate SCF and CCSD(T) calculations for the ^{3}F and ^{5}F states and optimized the polarization functions for the average energy of these two states.

Table 1. The cc-pV triple-zeta (*TZ*), quadruple-zeta (*QZ*) and quintuple-zeta (*5Z*) polarization functions

	f	*g*	*h*	*i*
3*d* and 4*s* valence correlation				
TZ	1.275220	0.630000		
	0.292750			
QZ	2.345000	1.535400	0.750000	
	0.670000	0.391185		
	0.191429			
5Z	3.682650	2.533680	1.843427	0.740000
	1.232480	0.816000	0.498898	
	0.412477	0.262802		
	0.138044			
3*s*, 3*p*, 3*d*, and 4*s* correlation				
TZ	2.744000	0.630000		
	0.980000			
	0.350000			
QZ	3.554446	3.446520	0.750000	
	1.487216	1.492000		
	0.622266	0.645887		
	0.260362			
5Z	5.511020	4.421637	4.305000	0.740000
	2.419236	2.106544	2.050000	
	1.062000	1.003594	0.976190	
	0.466198	0.478130		
	0.204653			

We first consider the valence cc-pV set, where only the four 3*d* and 4*s* electrons are correlated. The *spd* basis set is derived from our previously published average atomic natural orbital set [20]. The primitive set starts with the (21*s* 13*p* 8*d)* basis set optimized by Partridge [21]. It adds three diffuse p functions and one diffuse d function. The published [20] contraction is changed to allow 3*s* and 3*p* correlation; namely, the inner 16 *s* primitives are contracted to three functions, the inner 10 *p* primitives to two functions and the inner 4 *d* primitives to one function. Thus the valence basis set can be described as (21*s*16*p*9*d*)/[7*s*8*p*6*d*]. While the contraction coefficients are taken from an average of the ^{3}F and ^{5}F states, the contraction is so flexible, that using the ground-state ^{3}F orbitals would not make a significant difference. This valence set is used in all the cc-pV sets, only the polarization set is changed.

Adding another diffuse d function changes the CCSD(T) correlation energy by less than 2 cm^{-1}, therefore the f functions are the first polarization functions that we add. The TZ, QZ, and 5Z polarization series are 2*f*1*g*, 3*f*2*g*1*h*, and 4*f*3*g*2*h*1*i*, respectively. The even-tempered optimized exponents are given in Table 1. The entire basis set is given at http://ccf.arc.nasa.gov/~cbauschl/ti.basis.

It is known that correlation of the 3*s* and 3*p* electrons can affect the computed spectroscopic constants. This effect is largest for Sc and Ti and rapidly decreases as *Z* increases. We therefore consider a Ti basis set for 12-electron correlation treatments. There are several possible approaches to developing this set. The first is to simply use the four-electron valence basis set, assuming that there are sufficiently tight functions in the basis set, i.e., assume that the functions that correlated the 3*d* orbital also correlate the 3*s* and 3*p* orbitals, since the 3*d* orbital has a radial extent similar to the 3*s* and 3*p* orbitals. The second approach is to optimize functions for a 12-electron correlation treatment. This approach can be subdivided into optimizing additional polarization functions for 3*s* and 3*p* correlation, or optimizing all the polarization functions for a 12-electron treatment. Optimizing the 2*f*1*g*, 3*f*2*g*1*h*, and 4*f*3*g*2*h*1*i* cc-pV basis series at the 12-electron level results in exponents that are significantly larger than those found at the four-electron level. Since 3*d* and 4*s* correlation is expected to be more important than the 3*s* and 3*p* correlation for describing any bonding, this approach was rejected as it appeared to degrade the description of the valence correlation. Previously [22] for Ga we optimized a series of cc-pV sets for 4*s* and 4*p* correlation and then added a second cc-pV series for 3*d* correlation. For Ti 3*s* and 3*p* correlation, the TZ, QZ, and 5Z series would be 2*d*1*f*, 3*d*2*f*1*g*, and 4*d*3*f*2*g*1*h*. The addition of polarization d functions is not necessary since the valence set is very large; however, even adding only the f–h functions for 3*s* and 3*p* correlation to the valence set, results in a basis set that is much larger than needed since the functions for the 3*s* and 3*p* correlation overlap with the functions that describe the 3*d* and 4*s* correlation. On the basis of some experimentation, we conclude that the union of the basis sets for the 4- and 12-electron treatments contains one additional function, relative to the four-electron basis sets. For example the union of the 5Z valence set (4*f*3*g*2*h*1i) and the 3*s* and 3*p* correlation set (3*f*2*g*1*h*) is 5*f*4*g*3*h*1*i*. Therefore we adopt a TZ, QZ, and 5Z series of 3*f*1*g*, 4*f*3*g*1*h*, and 5*f*4*g*3*h*1*i*, respectively, for the 12-electron treatment. Since the function with the highest *l* value is derived from the valence set, the exponent is taken from the four-electron optimization. The remaining functions are optimized at the 12-electron level. These optimized even-tempered polarization functions are also given in Table 1.

4 Tests of the Ti basis set

The computed ^{3}F–^{5}F Ti separation is summarized in Table 2. When four electrons are correlated at the CCSD(T) level, the separations are very similar for the valence basis set and for the 3*s*, 3p, 3*d*, and 4*s* (3*s*3*p*) correlation set. The two extrapolation methods yield very similar results. We also note that n^{-3} extrapolation using the TZ and QZ basis sets (not shown) yields a value very similar to the two three-point approaches. When 12 electrons are correlated, the separation is reduced. The two different basis sets yield similar results. The two three-point extrapolation methods are in

Table 2. The Ti ^{3}F–^{5}F separation (eV). See text for an explanation of the abbreviations

Treatment	Basis	TZ	QZ	5Z	CBS[a]	CBS(α)[b]
4*e* CCSD(T)	Val	0.948	0.927	0.922	0.919	0.919
4*e* CCSD(T)	3*s*3*p*	0.948	0.933	0.927	0.921	0.918
12*e* CCSD(T)	Val	0.787	0.712	0.678	0.644	0.625
12*e* CCSD(T)	3*s*3*p*	0.772	0.707	0.676	0.645	0.625
12*e* MCPF	3*s*3*p*	0.784				
12*e* MCPF (DK)	3*s*3*p*[c]	0.930				
12*e* CCSD(T) + Rel					0.791	0.771
Expt[d](average *J*)						0.806

[a] CBS values computed using the three-point $n^{-4}+n^{-6}$ scheme

[b] CBS values computed using the three-point variable α scheme

[c] The contraction is taken from DK SCF calculations

[d] Ref. [12]

Table 3. Summary of TiCl spectroscopic constants

	r_e (Å)	D_e (eV)	w_e (cm^{-1})
Valence correlation treatment-valence basis set			
CCSD(T) TZ	2.315	4.167	387
CCSD(T) QZ	2.312	4.266	387
CCSD(T) 5Z	2.309	4.305	390
CCSD(T) CBS		4.341	
Valence correlation treatment-3*s*3*p* basis set			
CCSD(T) TZ	2.313	4.173	387
CCSD(T) QZ	2.311	4.270	388
CCSD(T) 5Z	2.309	4.306	390
CCSD(T) CBS		4.339	
Valence + Ti 3*s*3*p* correlation treatment-3*s*3*p* basis set			
CCSD(T) TZ	2.285	4.184	397
CCSD(T) QZ	2.279	4.304	396
CCSD(T) 5Z	2.274	4.357	400
CCSD(T) CBS		4.410	
MCPF TZ	2.292	4.157	398
MCPF(DK) TZ[a]	2.291	4.091	399

[a] The contraction is taken from DK SCF calculations

Table 4. Summary of TiH^{+} spectroscopic constants

	r_e (Å)	D_e (eV)	w_e (cm^{-1})
Valence correlation treatment-valence basis set			
CCSD(T) TZ	1.739	2.412	1700
CCSD(T) QZ	1.737	2.450	1700
CCSD(T) 5Z	1.737	2.464	1699
CCSD(T) CBS		2.477	
Valence correlation treatment-3*s*3*p* basis set			
CCSD(T) TZ	1.737	2.415	1706
CCSD(T) QZ	1.736	2.451	1703
CCSD(T) 5Z	1.736	2.464	1702
CCSD(T) CBS		2.476	
Valence + Ti 3*s*3*p* correlation treatment-valence basis set			
CCSD(T) TZ	1.714	2.398	1720
CCSD(T) QZ	1.707	2.462	1730
CCSD(T) 5Z	1.703	2.497	1745
CCSD(T) CBS		2.535	
Valence + Ti 3*s*3*p* correlation treatment-3*s*3*p* basis set			
CCSD(T) TZ	1.711	2.406	1726
CCSD(T) QZ	1.705	2.467	1736
CCSD(T) 5Z	1.702	2.498	1754
CCSD(T) CBS		2.531	
MCPF TZ	1.717	2.401	1725
MCPF(DK) TZ[a]	1.718	2.348	1721

[a] The contraction is taken from DK SCF calculations

reasonable agreement. Our experience has been that when the two extrapolation approaches differ, the $n^{-4}+n^{-6}$ approach is superior; thus we choose 0.645 eV as our best value for the ^{3}F–^{5}F Ti separation. We should note that the difference between the two three-point extrapolations also means that two-point extrapolation approaches [8, 9] using only the TZ and QZ basis sets have about 0.02 eV error. This is discussed further below.

The 12-electron MCPF separation is similar to the CCSD(T) result using the same basis set. The separation increases when scalar relativistic effects are included. Adding the MCPF relativistic effect to the 12-electron CBS CCSD(T) value leads to our best estimate, without including spin-orbit effects. This value is in excellent agreement with the *J*-averaged experimental separation. While the $n^{-4}+n^{-6}$ extrapolation yields a result that is in excellent agreement with experiment, the variable α CBS value is also in good agreement with experiment.

The spectroscopic constants (r_e, w_e, and D_e) for TiCl, TiH, and TiH^{+} are summarized in Tables 3–5. As expected, improving the basis set decreases r_e and increases D_e and w_e. The valence treatment results vary slightly between the two Ti basis sets. Adding Ti 3*s* and 3*p* correlation reduces r_e and increases D_e and w_e but the effects are relatively small. The effects are slightly larger for the cc-pV(3*s*3*p)* basis set than for the valence basis set, but overall the agreement between these two basis sets is good.

The MCPF results are in good agreement with the analogous CCSD(T) results. The relativistic effects at the MCPF level are relatively small, because the Ti *s* population has not changed dramatically when the first bond is formed. For other molecules these effects could be larger. For the systems considered in this work, the r_e and w_e values hardly change and the D_e values are slightly reduced.

For the valence correlation treatments, the two three-point extrapolation approaches yield very similar D_e values. The two-point n^{-3} extrapolation using the TZ and QZ basis sets is also in good agreement with the three-point approaches. This is true for both series of Ti basis sets. When the Ti 3*s* and 3*p* correlation is included, the same problems arise as found for the Ti atomic separations. The variable α results are about 0.03 eV larger than those obtained using the $n^{-4}+n^{-6}$ approach. The two-point n^{-3} results using the TZ and QZ basis sets have an error of 0.02 eV compared with the $n^{-4}+n^{-6}$ results. The problems encountered with Ti 3*s* and 3*p* correlation are about equally serious for both the valence and cc-pV(3*s*3*p*) Ti basis sets, i.e. extrapolation of the four-electron treatment of Ti is consistent with cc-pV sets for nontransition metals, while the 12-electron treatments do not extrapolate as well as found for other systems.

In previous work [23], we found that a variation in results between the different extrapolation approaches indicated some deficiency in a basis set; therefore, we performed many additional calculations on Ti, TiH, and

Table 5. Summary of TiH spectroscopic constants

	r_e (Å)	D_e (eV)	w_e (cm^{-1})
Valence correlation treatment-valence basis set			
CCSD(T) TZ	1.810	2.096	1514
CCSD(T) QZ	1.809	2.133	1510
CCSD(T) 5Z	1.809	2.146	1507
CCSD(T) CBS		2.157	
Valence correlation treatment-3*s*3*p* basis set			
CCSD(T) TZ	1.809	2.096	1516
CCSD(T) QZ	1.808	2.133	1512
CCSD(T) 5Z	1.808	2.146	1509
CCSD(T) CBS		2.157	
Valence + Ti 3*s*3*p* correlation treatment-valence basis set			
CCSD(T) TZ	1.781	2.119	1540
CCSD(T) QZ	1.774	2.176	1540
CCSD(T) 5Z	1.769	2.206	1543
CCSD(T) CBS		2.238	
Valence + Ti 3*s*3*p* correlation treatment-3*s*3*p* basis set			
CCSD(T) TZ	1.778	2.122	1543
CCSD(T) QZ	1.771	2.177	1537
CCSD(T) 5Z	1.767	2.206	1559
CCSD(T) CBS		2.237	
MCPF TZ	1.784	2.179	1543
MCPF(DK) TZ[a]	1.784	2.127	1543

[a] The contraction is taken from DK SCF calculations

TiH$^+$. The additional tests include using a larger *spd* primitive set, adding diffuse functions to the 3*s*3*p* basis set, adding additional tight functions to the valence and 3*s*3*p* basis sets, changing the number and *l* values of functions added to the valence set to create the 3*s*3*p* set, etc. However, none of these modifications yield similar results for all extrapolation methods for all three systems. While it is possible that some modification of the Ti basis set will improve the extrapolation using only the TZ and QZ basis set, currently the 3*s* and 3*p* effects are probably only computed correctly in those cases where the 5Z calculation is possible. For the transition-metal elements to the right of Ti, where 3*s* and 3*p* correlation is less important, this basis set extrapolation problem is probably best avoided by developing only valence correlation basis sets. This would also allow a more compact contraction of the *spd* spaces than used in this work.

At the CASSCF level, the difference between the nonrelativistic energy (*J*-averaged) and the lowest *J* level is 231.8 cm^{-1} for Ti ^{3}F, which compares favorably with experiment (222.5 cm^{-1}). The agreement is equally good for Ti$^+$ ^{4}F, 233.6 versus 225.0 cm^{-1}. Applying the same approach to TiCl, TiH, and TiH$^+$ yields molecular spin-orbit lowerings of 191.4, 165.7, and 170.5 cm^{-1}, respectively. For Cl we take the experimental [12] value. Using these values, the effect of spin-orbit effects on the dissociation energy can be computed.

Table 6. Summary of bond energies (eV)

	TiCl	TiH$^+$	TiH
CCSD(T) CBS	4.410	2.531	2.237
Zero-point energy	−0.025	−0.109	−0.097
Scalar rel(MCPF)	−0.066	−0.053	−0.052
Spin-orbit	−0.041	−0.008	−0.008
Best D_0	4.277	2.361	2.080
Expt	4.17 ± 0.11[a]	2.31 ± 0.11[b]	2.08 ± 0.09[c]

[a] Ref. [26], corrected to 0 K
[b] Ref. [24]
[a] Ref. [25], corrected to 0 K

The computed dissociation energies are summarized in Table 6. We take our CCSD(T) CBS value obtained with Ti 3*s* and 3*p* correlation as our best nonrelativistic D_e value. We correct for zero-point energy, scalar relativistic effects, and spin-orbit effects, yielding our best D_0 value. These values compare favorably with experiment [24–26]. In all three cases, theory agrees with experiment to within the experimental uncertainty. For TiCl and TiH$^+$, the treatments that include only Ti valence correlation agree better with experiment, but we believe this to be fortuitous, and that the true value is closer to the computed value including Ti 3*s* and 3*p* correlation. More accurate experimental values are required to test this speculation, however, regardless of the small difference between theory and experiment, it is encouraging that we have been able to compute such accurate bond energies for transition-metal-containing compounds without any experimental input.

We note that Baboul and Schlegel [27] computed a Ti-Cl bond energy of 4.17 eV using a modified G2 approach. This is in excellent agreement with experiment, and this approach benefits from some cancellation of errors; for example, the effect of Ti 3*s* and 3*p* correlation (0.071 eV) approximately cancels the sum of the scalar relativistic and spin-orbit effects (−0.107 eV). While it is encouraging that their modified G2 approach works so well, additional work is required before such approaches can be used routinely for transition-metal systems. We believe that our correlation-consistent basis sets can be used to compute accurate bond energies to help calibrate more approximate techniques.

5 Conclusions

Ti correlation-consistent basis sets are developed for the average of the ^{3}F and ^{5}F states. Basis sets for Ti 3*d* and 4*s* correlation and for Ti 3*s*, 3*p*, 3*d*, and 4*s* correlation are developed. Somewhat surprisingly, the two basis sets yield similar results for 4- or 12-electron treatments of Ti. The extrapolated results for the Ti ^{3}F–^{5}F separation and the TiCl, TiH, and TiH$^+$ bond energies suggest that the procedure of using the average energy of the low-lying states to optimize the polarization functions is a viable method for developing correlation-consistent basis sets for the first row transition-metal atoms, especially for those on the right-hand side of the row where 3*s* and 3*p* correlation can probably be neglected.

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