

**GROUP IIIa HYDRIDES  $XH_2$  AND  $XH_2^-$  (X = B, Al, Ga): ELECTRON AFFINITIES AND SINGLET-TRIPLET SPLITTINGS REVISITED**Ivan ČERNUŠÁK<sup>a1,\*</sup>, Alena ZAVAŽANOVÁ<sup>a,b</sup>, Juraj RAAB<sup>a2</sup> and Pavel NEOGRÁDY<sup>a3</sup>

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*This paper is dedicated to our teachers, colleagues and friends Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays. We are happy to celebrate their contribution to the formation of Czechoslovak school of quantum chemistry – the centre of scientific excellence in the heart of Europe.*

Geometries, electron affinities (EA) and singlet-triplet (S-T) splittings of  $XH_2/XH_2^-$  molecules (X = B, Al, Ga) are calculated by coupled-cluster methods, using the sequence of basis sets. The EA values and S-T splittings for aluminium and gallium dihydrides are an order of magnitude larger (in absolute values) than those for boron. For boron and aluminium dihydrides, two types of extrapolations towards complete basis set limit are applied, leading to EA = 0.24 eV, ST = -0.01 eV ( $BH_2$ ), and EA = 1.10 eV, ST = -0.62 eV. The best calculated values for gallium dihydrides are EA = 1.13 eV and ST = -0.74 eV. All three S-T splittings favour singlet as the ground state, although the S-T splittings of  $BH_2^-$  is exceptionally small. In addition, vertical electron affinities and vertical electron detachments are reported for these molecules.

**Keywords:** Hydrides; Electron affinity; Singlet-triplet splitting; Coupled cluster method; *Ab initio* calculations; Boron; Aluminium; Gallium.

Despite rapid development of highly sophisticated computational techniques for calculations of correlation energy, the accurate predictions of excited states, singlet-triplet splitting and electron affinities are still a challenge for current theoretical chemistry. The principal requirements for high-quality calculations of these properties are: inclusion of electron correlation at computational limits, balanced treatment of both ion and neutral molecule and a large flexible basis set. In practice, one can only approach these criteria due to limitations of computational resources.

Small hydrides  $\text{XH}_2$  (X being a p-block element) and their negative ions rank among compounds that were intensively studied in the past two decades<sup>1-3</sup> thanks to their industrial application in semiconductor technology, light emitting diodes<sup>4</sup>, solar cells, lasers and chemical vapour deposition processes. In particular, gallium-containing molecules are important in this context. Group IIIa dihydrides are interesting also from the theoretical point of view since they can be products of crossed-molecular-beams reaction<sup>5</sup>:  $\text{XH} + \text{XH}^- \rightarrow \text{XH}_2^- + \text{X}^{\cdot}$ .

Triatomic  $\text{XH}_2^-$  systems (X = B, Al, Ga) with six valence electrons were studied by several authors<sup>3,6,7</sup> using *ab initio* methods. The early study of Pople and coworkers<sup>6</sup> ( $\text{BH}_2/\text{BH}_2^-$  and also  $\text{AlH}_2/\text{AlH}_2^-$ ) was limited to geometry optimization using Hartree-Fock (HF) method and a small basis of double- $\zeta$  quality. Singlet-triplet splittings and electron affinities were evaluated at fourth-order Many Body Perturbation Theory (MBPT(4)) levels. However, this approach led to contradictory singlet-triplet ordering, as was shown later in Multireference Configuration Interaction with Single and Double Excitations (MRCISD) studies by Cremer *et al.*<sup>3</sup> and Gu *et al.*<sup>7</sup> Both groups obtained very small S-T splitting, of the order of *ca* 100  $\text{cm}^{-1}$ ; this quantity thus still presents a challenge for computational chemistry. Spectroscopic properties and rovibronic energies of neutral  $\text{BH}_2$  were studied by Kolbuszewski *et al.*<sup>8</sup> Gallium dihydride was also part of Cremer's study<sup>3</sup> but the relativistic effects were treated only *via* effective core potentials. Recently,  $\text{AlH}_2$  and  $\text{GaH}_2$  were included in vibrational study by Pullumbi *et al.*<sup>9</sup> (geometries, frequencies and dipole moments), and gallium dihydride in a combined experimental (EPR) and theoretical study by Knight *et al.*<sup>2</sup> Thus, the series  $\text{BH}_2/\text{BH}_2^-$ ,  $\text{AlH}_2/\text{AlH}_2^-$ ,  $\text{GaH}_2/\text{GaH}_2^-$  is scattered across different papers at different levels of accuracy and we feel that comprehensive treatise (both experimental and theoretical) is missing.

The experimental and theoretical efforts resulted in relatively limited accumulation of information, the important relevant experimental data for these species being scarce. In this paper we present the systematic examination of the series  $\text{BH}_2$ ,  $\text{AlH}_2$ ,  $\text{GaH}_2$  and their negative ions, using *ab initio* Coupled Clusters method (CCSD and CCSD(T))<sup>10,11</sup> including scalar relativistic effects for gallium dihydride. In particular, we focus on the geometries, electron affinities and singlet-triplet splittings. These properties are interesting also from the theoretical point of view since their analysis can contribute to better understanding of chemical reactivity and correlation effects in these systems. For  $\text{BH}_2/\text{BH}_2^-$  and  $\text{AlH}_2/\text{AlH}_2^-$  we also provide estimates of the complete basis set (CBS) limit based on the series of three correlation-

consistent basis sets, while for  $\text{GaH}_2/\text{GaH}_2^-$  our primary aim was to investigate the scalar relativistic effects and different freezing of inner shell orbitals in correlated calculations. In addition to the (adiabatic) properties mentioned above, we report also vertical electron detachment, vertical electron affinities and vertical singlet-triplet splittings.

## METHODS

The popular version of the coupled cluster (CC) method, the CCSD(T) approach<sup>10–16</sup> was used in this study. In the majority of the optimizations ( $\text{BH}_2/\text{BH}_2^-$  and  $\text{AlH}_2/\text{AlH}_2^-$ ), we have used ACESII<sup>17</sup> and Gaussian 98<sup>18</sup> programs. The  $\text{GaH}_2/\text{GaH}_2^-$  part was treated slightly differently, using the MOLCAS program system<sup>19</sup>; this will be specified in the next paragraphs.

For the determination of equilibrium geometries and energy quantities, we have adopted the following strategy:

At the first stage all the geometries were predetermined at the second-order Many Body Perturbation Theory, MBPT(2)/ANO-S level (for neutrals we have used unrestricted Hartree–Fock (UHF) reference), using gradient optimization<sup>17,18</sup>. The following ANO basis sets<sup>20</sup> were chosen for these optimizations and frequency calculations:  $\text{BH}_2/\text{BH}_2^-$  [5s3p2d/3s2p],  $\text{AlH}_2/\text{AlH}_2^-$  [7s5p3d/3s2p],  $\text{GaH}_2/\text{GaH}_2^-$  [9s7p3d/3s2p]. Core electrons were frozen in correlated calculations, K shell for boron, K, L shells for aluminium and K, L, M shells for gallium.

At the second stage the  $\text{BH}_2/\text{BH}_2^-$  and  $\text{AlH}_2/\text{AlH}_2^-$  structures were reoptimized at the CCSD(T)<sup>14–16</sup> level. In order to evaluate the basis set effects, we have used also correlation consistent aug-cc-pvtz and aug-cc-pvqz basis sets<sup>21–24</sup>. To estimate the core-valence correlation effects for  $\text{BH}_2/\text{BH}_2^-$ , additional CCSD(T)/aug-cc-pCvtz and CCSD(T)/aug-cc-pCvqz<sup>23</sup> calculations were performed with all electrons correlated. Finally, we have used the CCSD(T)/aug-cc-pvqz geometries ( $\text{BH}_2/\text{BH}_2^-$  and  $\text{AlH}_2/\text{AlH}_2^-$ ) in single-point restricted open-shell Hartree–Fock (ROHF) based CCSD(T)/aug-cc-pv5z calculations<sup>19</sup> of EAs and S-T splittings.

It is known from the literature<sup>3,7</sup> that the EAs and the S-T splitting in boron hydrides are an order of magnitude smaller than in aluminium and gallium hydrides. Therefore, we have refined the zero-point energy (ZPE) corrections for boron hydrides at the highest accessible level, CCSD(T)/aug-cc-pvqz, to minimize the effect of possible ZPE inaccuracies on EA and S-T splitting. The ZPEs for aluminium and gallium hydrides were calculated at the MBPT(2)/aug-cc-pvtz level.

At the third stage we have reoptimized the geometries of  $\text{GaH}_2/\text{GaH}_2^-$  numerically from the energy grid around the expected minima, using the CCSD(T) method including Douglas–Kroll (DK) scalar relativistic correction<sup>19</sup>. To make some more comparisons, we have used the following basis sets for gallium: ANO-S [9s7p3d/3s2p]<sup>25</sup> for nonrelativistic and uncontracted ANO-S (17s15p9d/7s3p)<sup>25</sup> for relativistic calculations. In addition, for DK calculations we have selected also the Ga.Pol.DK set<sup>26</sup> derived recently. This basis set consists of (15s12p8d2f) primitives contracted to [9s7p4d1f]. Finally, we have performed single-point calculations of electron affinities and S-T splittings, using the aug-cc-pv5z-DK<sup>27</sup> basis with two versions of freezing of inner-shell orbitals – KL3p<sup>2</sup>p<sup>6</sup> and KL3p<sup>2</sup> shells frozen on gallium, respectively. The latter choice may have a significant impact on some properties of light transition metal-containing molecules, as indicated in a recent paper of Urban and Sadlej<sup>28</sup>.

For the CBS extrapolations, we have applied the same technique as in our recent study<sup>29</sup>. The first approach is based on the equation proposed by Helgaker<sup>30,31</sup>. It employs the energies from the sequence of correlation consistent basis sets

$$E(X) = E_{\text{CBS}} + A/X^3, \quad (1)$$

where  $X$  is cardinal number directly related to highest angular momentum basis function. Peterson *et al.*<sup>32</sup> proposed a mixed exponential/Gaussian three-point formula

$$E(X) = E_{\text{CBS}} + \frac{B}{\exp(X-1)} + \frac{C}{\exp[(X-1)^2]}. \quad (2)$$

In connection with photoelectron spectra, three quantities might be of interest: vertical electron detachment (VEDE), adiabatic electron affinity (EA) and vertical electron affinity (VEA). Assuming molecule A, VEDE is calculated at the geometry  $\mathbf{g}^-$  of its anion  $\text{A}^-$ :

$$\text{VEDE} = E(\text{A}, \mathbf{g}^-) - E(\text{A}^-, \mathbf{g}^-). \quad (3)$$

EA includes also the effect of geometry relaxation ( $\mathbf{g}$  denotes the geometry of the neutral molecule A):

$$EA = E(A, \mathbf{g}) - E(A^-, \mathbf{g}^-), \quad (4)$$

while in VEA one assumes the geometry of the neutral molecule also for the anion:

$$VEA = E(A, \mathbf{g}) - E(A^-, \mathbf{g}). \quad (5)$$

It is useful to calculate all three quantities since the experimental results may depend on the nature of the measurement, *e.g.* ultrafast techniques can, in principle, provide *vertical* data. Similarly, we can calculate adiabatic S-T splitting

$$ST = E(S) - E(T), \quad (6)$$

*i.e.*, positive value for S-T splitting indicates the triplet is more stable than singlet.

## RESULTS AND DISCUSSION

Optimized geometries and zero-point energies (including the harmonic wavenumbers) are summarized in Tables I–III. Although the geometries are usually not very sensitive to the level of approximations used in this paper,

TABLE I  
Geometries<sup>a</sup> and ZPEs<sup>b</sup> of BH<sub>2</sub>/BH<sub>2</sub><sup>-</sup>

B-H	HBH	B-H	HBH	B-H	HBH	Method/Basis set
<sup>1</sup> A <sub>1</sub>		<sup>3</sup> B <sub>1</sub>		<sup>2</sup> A <sub>1</sub>		
1.242	104.2	1.208	128.9	1.190	128.6	CCSD(T)/[5s3p2d/2s2p]
1.2410	105.1	1.2064	129.3	1.1894	128.9	CCSD(T)/aug-cc-pvtz
1.2388	105.2	1.2046	129.4	1.1877	128.9	CCSD(T)/aug-cc-pvqz

<sup>a</sup> Bond lengths (in Å) and bond angles (in °). <sup>b</sup> CCSD(T)/aug-cc-pvqz ZPEs (in kJ mol<sup>-1</sup>) and harmonic wavenumbers (in cm<sup>-1</sup>), <sup>1</sup>A<sub>1</sub>: ZPE = 33.28, ω<sub>1</sub>(a<sub>1</sub>) = 1054.1, ω<sub>2</sub>(a<sub>1</sub>) = 2226.5, ω<sub>3</sub>(b<sub>2</sub>) = 2283.2; <sup>3</sup>B<sub>1</sub>: ZPE = 35.67, ω<sub>1</sub>(a<sub>1</sub>) = 920.8, ω<sub>2</sub>(a<sub>1</sub>) = 2451.4, ω<sub>3</sub>(b<sub>2</sub>) = 2591.9; <sup>2</sup>A<sub>1</sub>: ZPE = 36.37, ω<sub>1</sub>(a<sub>1</sub>) = 1011.7, ω<sub>2</sub>(a<sub>1</sub>) = 2592.5, ω<sub>3</sub>(b<sub>2</sub>) = 2756.0

TABLE II  
 Geometries<sup>a</sup> and ZPEs<sup>b</sup> of AlH<sub>2</sub>/AlH<sub>2</sub><sup>-</sup>

Al-H	HAlH	Al-H	HAlH	Al-H	HAlH	Method/Basis set
<sup>1</sup> A <sub>1</sub>		<sup>3</sup> B <sub>1</sub>		<sup>2</sup> A <sub>1</sub>		
1.686	95.4	1.623	118.0	1.599	118.5	CCSD(T)[7s5p3d/3s2p]
1.6929	95.1	1.6263	118.0	1.6010	118.4	CCSD(T)/aug-cc-pvtz
1.6862	95.2	1.5962	117.5	1.5969	118.3	CCSD(T)/aug-cc-pvqz

<sup>a</sup> See footnotes in Table I. <sup>b</sup> MBPT(2)/aug-cc-pvtz ZPEs (in kJ mol<sup>-1</sup>) and harmonic wavenumbers (in cm<sup>-1</sup>), <sup>1</sup>A<sub>1</sub>: ZPE = 23.24, ω<sub>1</sub>(a<sub>1</sub>) = 822.7, ω<sub>2</sub>(a<sub>1</sub>) = 1525.8, ω<sub>3</sub>(b<sub>2</sub>) = 1537.1; <sup>3</sup>B<sub>1</sub>: ZPE = 25.68, ω<sub>1</sub>(a<sub>1</sub>) = 735.7, ω<sub>2</sub>(a<sub>1</sub>) = 1773.9, ω<sub>3</sub>(b<sub>2</sub>) = 1784.1; <sup>2</sup>A<sub>1</sub>: ZPE = 27.54, ω<sub>1</sub>(a<sub>1</sub>) = 784.6, ω<sub>2</sub>(a<sub>1</sub>) = 1895.9, ω<sub>3</sub>(b<sub>2</sub>) = 1923.9

 TABLE III  
 Geometries<sup>a</sup> and ZPEs<sup>b</sup> of GaH<sub>2</sub>/GaH<sub>2</sub><sup>-</sup>

Ga-H	HGaH	Ga-H	HGaH	Ga-H	HGaH	Method/Basis set
<sup>1</sup> A <sub>1</sub>		<sup>3</sup> B <sub>1</sub>		<sup>2</sup> A <sub>1</sub>		
KLM electrons frozen						
1.728	93.7	1.631	119.6	1.608	119.9	CCSD(T)/[9s7p3d/3s2p]
1.727	93.9	1.621	119.8	1.605	120.0	CCSD(T)/(17s15p9d/7s3p)
1.727	93.7	1.621	119.8	1.600	120.1	CCSD(T) + DK/(17s15p9d/7s3p)
KL3s <sup>2</sup> p <sup>6</sup> electrons frozen						
1.704	93.9	1.605	120.1	1.587	120.3	CCSD(T)/[9s7p3d/3s2p]
1.702	94.0	1.601	120.4	1.584	120.6	CCSD(T)/(17s15p9d/7s3p)
1.705	94.1	1.604	120.6	1.589	120.5	CCSD(T)/Pol
1.6993	93.8	1.5889	120.8	1.5759	120.8	CCSD(T) + DK/(17s15p9d/7s3p)
1.7040	93.9	1.5961	120.9	1.5811	120.8	CCSD(T) + DK/Pol.DK

<sup>a</sup> See also footnotes in Table I. <sup>b</sup> MBPT(2)/aug-cc-pvtz ZPEs (in kJ mol<sup>-1</sup>) and harmonic wavenumbers (in cm<sup>-1</sup>), <sup>1</sup>A<sub>1</sub>: ZPE = 23.63, ω<sub>1</sub>(a<sub>1</sub>) = 814.2, ω<sub>2</sub>(a<sub>1</sub>) = 1560.2, ω<sub>3</sub>(b<sub>2</sub>) = 1575.5; <sup>3</sup>B<sub>1</sub>: ZPE = 26.55, ω<sub>1</sub>(a<sub>1</sub>) = 726.1, ω<sub>2</sub>(a<sub>1</sub>) = 1849.4, ω<sub>3</sub>(b<sub>2</sub>) = 1863.0; <sup>2</sup>A<sub>1</sub>: ZPE = 28.16, ω<sub>1</sub>(a<sub>1</sub>) = 775.2, ω<sub>2</sub>(a<sub>1</sub>) = 1948.0, ω<sub>3</sub>(b<sub>2</sub>) = 1984.5

we are presenting in detail their convergence properties mainly because of the lack of experimental data. Control characteristics of correlated calculations, *viz.* spin contamination and largest  $T_1$  and  $T_2$  amplitudes from CCSD, are summarized in Table IV. The former is an indication of the quality of the open-shell reference wavefunction, the latter are useful tools for judging the reliability of single-reference CC approach<sup>29,33</sup>. Electron affinities, some related vertical quantities and singlet-triplet splittings are presented in Tables V–VII. In the following paragraphs, we will deal with each pair neutral/anion separately, while the vertical quantities will be discussed together at the end.

### $BH_2 / BH_2^-$

Boron dihydride and its anion are the most frequently studied system in our set. Judging from the geometries in our sequence of methods and basis sets (Table I), the B–H bonds are converged within 0.001–0.003 Å and HBH angles within 0.1°. Our best B–H and HBH data for singlet and triplet agree nicely with MRCISD results of Gu *et al.*<sup>7</sup> (B–H = 1.2369 Å, HBH = 105.7° for  $^1A_1$ ; B–H = 1.2034 Å, HBH = 129.5° for  $^3B_1$ ). The agreement with the DFT-NLDA results of Cremer *et al.*<sup>3</sup> (B–H = 1.259 Å, HBH = 101.7° for  $^1A_1$ ; B–H = 1.210 Å, HBH = 132.3° for  $^3B_1$ ) is less satisfactory. We stress that both groups used comparable large triple- $\zeta$  bases. However, the CASSCF geome-

TABLE IV  
Control characteristics of correlated calculations: largest  $t_i^a$  or  $t_{ij}^{ab}$  amplitudes and  $\tau_1$  diagnostics (CCSD/aug-cc-pv5z data)

	$ t_{\max} $	Type	$\tau_1$
$^1A_1 BH_2^-$	0.067	biexcitation	0.01238
$^3B_1 BH_2^-$	0.096	monoexcitation	0.03472
$^2A_1 BH_2$	0.025	biexcitation	0.01560
$^1A_1 AlH_2^-$	0.056	biexcitation	0.01930
$^3B_1 AlH_2^-$	0.043	monoexcitation	0.02720
$^2A_1 AlH_2$	0.038	monoexcitation	0.02039
$^1A_1 GaH_2^-$	0.057	biexcitation	0.02003
$^3B_1 GaH_2^-$	0.081	monoexcitation	0.02633
$^2A_1 GaH_2$	0.052	monoexcitation	0.02002

try for singlet and triplet from ref.<sup>3</sup> is noticeably off (B–H = 1.284 Å, HBH = 102.7° for <sup>1</sup>A<sub>1</sub>; B–H = 1.234 Å, HBH = 126.2° for <sup>3</sup>B<sub>1</sub>). Apparently, electron correlation treatment is insufficient in both DFT-NLDA and CASSCF. Our equilibrium CCSD(T)/aug-cc-pvqz bond length and bond angle for radical <sup>2</sup>A<sub>1</sub> match perfectly the MRCISD data of Kolbuszewski *et al.*<sup>8</sup> (1.1875 Å and 129.0°). In both open-shell cases, the spin contamination in our UHF-based

TABLE V  
CCSD(T) electron affinities, vertical quantities and singlet-triplet splittings of BH<sub>2</sub>/BH<sub>2</sub><sup>-</sup> systems (in eV). Last three rows refer to SCF, CCSD and CCSD(T), respectively, with the aug-cc-pv5z basis set

Basis	EA	EA <sub>ZPE</sub> <sup>a</sup>	VEA	VEDE	S-T <sup>b</sup>	S-T <sub>ZPE</sub> <sup>a</sup>
aug-cc-pvtz	0.2194	0.2266	0.2127	0.2264	0.0200	-0.0048
aug-cc-pCvtz	0.2143	0.2216	–	–	0.0294	0.0046
aug-cc-pvqz	0.2294	0.2367	0.2228	0.2364	0.0146	-0.0101
aug-cc-pCvqz	0.2296	0.2368	–	–	0.0263	0.0015
aug-cc-pv5z	-0.4307	–	-0.4289	-0.4167	0.6081	–
	0.1735	–	0.1691	0.1830	0.0422	–
	0.2314	0.2386	0.2253	0.2399	0.0076	-0.0172

<sup>a</sup> ZPE corrected (CCSD(T)/aug-cc-pvqz), see footnote *b* in Table I. <sup>b</sup> Other sources: 0.0460 (ref.<sup>3</sup>), 0.0443 (ref.<sup>7</sup>).

TABLE VI  
CCSD(T) electron affinities, vertical quantities and singlet-triplet splittings of AlH<sub>2</sub>/AlH<sub>2</sub><sup>-</sup> systems (in eV). Last three rows refer to SCF, CCSD and CCSD(T) with the aug-cc-pv5z basis set

Basis	EA	EA <sub>ZPE</sub> <sup>a</sup>	VEA	VEDE	S-T	S-T <sub>ZPE</sub> <sup>a</sup>
aug-cc-pvtz	1.0488	1.0934	0.7499	1.3548	-0.5867	-0.6124
aug-cc-pvqz	1.0526	1.0971	0.7582	1.3561	-0.5950	-0.6207
aug-cc-pv5z	0.0237	–	-0.2524	0.4057	0.0295	–
	1.0002	–	0.7133	1.3254	-0.5747	–
	1.0575	1.1021	0.7723	1.3744	-0.5942	-0.6199

<sup>a</sup> ZPE corrected, see footnote *b* in Table II.



CCSD(T)/aug-cc-pvqz runs using ACESII<sup>17</sup> was marginal ( $\hat{S}^2$  for  ${}^2A_1$  0.754, for  ${}^3B_1$  2.009).

The convergence of the EA to complete basis set limit (Table V, second row) is very good, while the S-T splittings decrease monotonically. For both the EAs and S-T splittings, correlation effects are tremendously important. For illustration, we give our “best” aug-cc-pv5z data in detail: the correlation contribution to electron affinity going from SCF to CCSD is quite large, 0.6042 eV, *i.e.*, the anion is unbound at the SCF level. Although the effect of triple excitations is only *ca* 10% of the CCSD, it is still non-negligible and stabilizes the anion by additional *ca* 0.0579 eV. The situation for S-T splitting is reversed: while at the SCF level the triplet is strongly preferred (ST = 0.6081 eV), the CCSD contribution lowers it by 0.5659 eV, pushing the singlet closer to the triplet. Moreover, the contribution of triple excitations further reduces the gap by 0.0346 eV to a very small value (Table V). Analysis of CCSD excitation amplitudes (Table IV) indicates that the singlet and doublet are represented very well within the single-determinant ROHF-CCSD(T) approach. The most significant control characteristics that could *possibly* affect the S-T splitting are those for  ${}^3B_1$  ( $BH_2^-$ ). The pertinent values of the  $t_1$  amplitude corresponding to single excitation from non-bonding  $n_\alpha$  to antibonding  $\pi_\alpha^*$  orbital for the triplet are still satisfactorily small, while  $\tau_1$  diagnostics is on the edge of acceptance. In other words, our ROHF-CCSD(T) approach is still acceptable, even though not

TABLE VII

CCSD(T) electron affinities, vertical quantities and S-T splittings of  $GaH_2/GaH_2^-$  systems (in eV). Last three rows refer to SCF, CCSD and CCSD(T) with the aug-cc-pv5z basis set

Basis	EA	EA <sub>ZPE</sub> <sup>a</sup>	VEA	VEDE	S-T	S-T <sub>ZPE</sub> <sup>a</sup>
(17s15p9d/7s3p) <sup>b</sup>	0.9965	1.0435	–	–	–0.6610	–0.6913
(17s15p9d/7s3p)	1.0032	1.0501	0.5979	1.4184	–0.7042	–0.7345
Pol <sup>b</sup>	1.0497	1.0966	–	–	–0.6909	–0.7212
Pol.DK	1.0596	1.1066	0.6643	1.4682	–0.7374	–0.7677
aug-cc-pv5z-DK	1.0928	1.1398	0.7573	1.5579	–0.7042	–0.7345
aug-cc-pv5z-DK <sup>c</sup>	0.1528	–	–	–	–0.1927	–
	1.0098	–	–	–	–0.6809	–
	1.0862	1.1331	–	–	–0.7108	–0.7411

<sup>a</sup> ZPE corrected, see footnote *b* in Table III. <sup>b</sup> Non-relativistic calculation. <sup>c</sup> Only KL3s<sup>2</sup> electrons frozen.

perfect. It is interesting that both MRCISD results<sup>3,7</sup> agree nicely with our CCSD S-T splitting, indicating the importance of connected triples (missing in MRCISD). To explain the observed difference between the cited and our results, one should consider both the basis-set effects and inclusion of connected triples in correlated calculation. Using a less flexible basis set, one can expect triplet preference (*i.e.*, a larger gap) due to smaller coulombic repulsion between valence electrons (see also the discussion in the paper of Cremer *et al.*<sup>3</sup>). Our final basis set (aug-cc-pv5z) is substantially more diffuse and flexible than those used in refs<sup>3,7</sup>, thus favoring equally the singlet and triplet. Our results confirm that the S-T splitting in  $\text{BH}_2^-$  is a very small quantity, and indicate that further improving the method/basis set would probably favour the singlet even more. For instance, we have calculated S-T splitting, using the fully iterative CCSDT/aug-cc-pvtz method, and the result (0.0166 eV) is lower than the CCSD(T)/aug-cc-pvtz one by 0.0054 eV. Finally, the core-valence effects can be important for such a small system like  $\text{BH}_2/\text{BH}_2^-$ . We have estimated the core-valence effects (using aug-cc-pCvtz and aug-cc-pCvqz bases), which amount to *ca* 0.01 eV for S-T splitting and are practically negligible for EA (-0.0051 eV for aug-cc-pCvtz and -0.0001 eV for aug-cc-pCvqz basis set, respectively). Equations (1) and (2) yielded the following CBS limits (ZPE included): 0.2426 and 0.2397 eV for EA and -0.0185 and -0.0214 eV for S-T splitting. Thus, our (averaged) recommended value for EA is 0.241 eV. S-T splitting is a very small and rather sensitive quantity with respect to both the method and basis set (especially due to the portion of correlation energy included) and oscillates around zero. If we include also core-valence correction we can arrive at the final estimate of the CBS limit for the S-T splitting -0.010 eV.

### $\text{AlH}_2 / \text{AlH}_2^-$

The geometry of the neutral  ${}^2\text{A}_1$  state agrees very well with recent CCSD(T) data of Pullumbi *et al.*<sup>9</sup> This is not surprising since the basis sets are of comparable quality. Similarly, the agreement with CASSCF data of Cremer *et al.*<sup>3</sup> is worse for anionic states. They used a smaller, less flexible basis set, leading to overestimated bond lengths (by about 0.03–0.05 Å). Our aug-cc-pvtz and aug-cc-pvqz geometries seem to be acceptably converged, with the exception of the  ${}^3\text{B}_1$  state for which we have found a slightly larger difference between the triple and quadruple bases. In both open-shell cases, the spin contamination was marginal ( $\hat{S}^2$  for  ${}^2\text{A}_1$  0.754, for  ${}^3\text{B}_1$  2.004). Also the control characteristics for aluminium species (Table IV) are small.

Electron affinities (both pure electron and ZPE-corrected) exhibit stable converging pattern (Table VI); the same holds for S-T splittings. Again, electron correlation is very important, although the ratio of individual contributions is slightly different from the  $\text{BH}_2/\text{BH}_2^-$  system (larger CCSD contribution, smaller triples). Other relevant theoretical data<sup>3</sup> are S-T splittings at MRCISD(Q)/TZP (-0.6201 eV) and DFT/TZ2P (-0.5290 eV) levels. Both include ZPE corrections calculated at the CASSCF/TZP level. Our ZPE-corrected S-T splittings are significantly larger (by about 0.07–0.10 eV). This difference is probably a combined effect of the method/basis set and geometry deficiency in ref.<sup>3</sup> We could not investigate core-correlation effects since the pertinent aug-cc-pCvXz basis has not been available yet for Al. According to Eqs (1) and (2), the extrapolation of the ZPE-corrected EA leads to the values 1.1030 and 1.1050 eV. The respective S-T splittings are -0.6235 and -0.6194 eV. Averaging these two values, we estimate the CBS limits at 1.104 eV (EA) and -0.621 eV (S-T).

### $\text{GaH}_2 / \text{GaH}_2^-$

While the bond angles are less sensitive to the number of correlated orbitals, bond lengths obtained with frozen KLM shells differ from  $\text{KL3s}^2\text{p}^6$  freezing by ca 0.02 Å. Therefore, we will discuss data based only on the latter case. Scalar relativistic effects on geometry are small; we have observed the most apparent shift for the  $^3\text{B}_1$  ( $\text{GaH}_2^-$ ) state (Table III, *cf.* rows for the Pol.DK and Pol basis sets). However, even the largest difference in bond distance amounts only to 0.008 Å and in bond angle to 0.3°. Other authors have reported  $\text{Ga-H} = 1.757$  Å,  $\text{HGaH} = 94.9^\circ$  ( $^1\text{A}_1$ ),  $\text{Ga-H} = 1.635$  Å,  $\text{HGaH} = 119.9^\circ$  ( $^3\text{B}_1$ )<sup>3</sup> and  $\text{Ga-H} = 1.628$  Å,  $\text{HGaH} = 118.7^\circ$  ( $^2\text{A}_1$ )<sup>2</sup>. Similarly to aluminium hydrides, all bond lengths are overestimated (by 0.02–0.04 Å) by these authors, while bond angles for the singlet and doublet are smaller and for the triplet larger than our best CCSD(T)/Pol.DK; however, the differences do not exceed  $\pm 2^\circ$ . Since we used a more elaborate method and/or larger basis sets and the oscillations within our series are negligibly small, we regard our geometries as more reliable.

As in the previous two cases, electron correlation plays a crucial role in correct prediction of EA and S-T splitting (*cf.* the last three rows of Table VII). Scalar relativistic effects are rather limited for EAs: 0.007 eV for smaller (17s15p9d/7s3p) and 0.01 eV for larger Pol.DK values. In S-T gaps the relativistic contributions are larger and range from -0.043 to -0.036 eV (Table VII). Despite the heterogeneous basis sets, the CCSD(T) EA values in the second column of Table VII ( $\text{KL3s}^2\text{p}^6$  frozen electrons) converge well

and our “best” value corrected for ZPE is 1.140 eV. Incidentally, the S-T splittings for (17s15p9d/7s3p) basis and for aug-cc-pv5z-DK are the same (within the accuracy presented). Correlating also the 3p<sup>6</sup> electrons on Ga atom decreases the “best” calculated value of EA by 0.007 eV and thus the ultimate calculated value is 1.133 eV. Concerning the S-T splitting, the sequence does not seem to be under perfect numerical control. Nevertheless, since the two aug-cc-pv5z-DK values do not differ significantly, we can suggest the (ZPE-corrected) estimate of -0.741 eV. As in both previous systems, our S-T splitting obtained with a large flexible basis set differs significantly from the MRCISD(Q)/TZP value<sup>3</sup> of -0.7025 eV.

To our knowledge, there is no direct experimental data for EAs and S-T splittings for group IIIa dihydrides. However, there is indirect EA[AlH<sub>2</sub>] = 1.22 ± 0.42 eV<sup>34</sup>, obtained from the theoretical gas-phase acidity and experimental data. Our “best” electron affinity of 1.06 eV lies within error bars of the electron affinity from ref.<sup>34</sup>

### *Vertical Quantities*

VEA and VEDE exhibit different patterns for BH<sub>2</sub>/BH<sub>2</sub><sup>-</sup> compared with AlH<sub>2</sub>/AlH<sub>2</sub><sup>-</sup> and GaH<sub>2</sub>/GaH<sub>2</sub><sup>-</sup> (due to the fact that triplet BH<sub>2</sub><sup>-</sup> was considered to be the ground state on the basis of calculations without ZPE). In boron dihydrides, the differences between EA, VEA and VEDE are smaller due to conformity in doublet and triplet geometries amounting to ±0.006 eV. Also the trends in correlation contributions are similar: a large and stabilizing net CCSD contribution and a smaller destabilizing effect of triples. On the other hand, the vertical quantities for AlH<sub>2</sub>/AlH<sub>2</sub><sup>-</sup> and GaH<sub>2</sub>/GaH<sub>2</sub><sup>-</sup> are based on distinctively different geometries of singlet and doublet and, consequently, they reflect different trends in geometry relaxation upon electron attachment or detachment.

### CONCLUSIONS

Calculations of electron affinities and S-T splittings present a computational challenge even for small molecules since they include vastly different many-electron systems. In our study we have attempted to demonstrate that CCSD(T) methods, when applied in controllable way, can provide molecular data and contribute to accumulation of knowledge on both closed- and open-shell systems not easily amenable to experiment. Our predictions for BH<sub>2</sub>/BH<sub>2</sub><sup>-</sup> and AlH<sub>2</sub>/AlH<sub>2</sub><sup>-</sup> are based on highly correlated calculations, using the sequence of aug-cc-pvXz basis sets (X = 3, 4, 5). From two types of

CBS extrapolations, we have obtained ZPE-corrected electron affinities and S-T splittings that do not differ in absolute values more than 0.003 and 0.004 eV, respectively. Thus, both extrapolation procedures provide fairly stable values for these quantities. The respective estimates for  $\text{GaH}_2/\text{GaH}_2^-$  systems are the first data that provide both the relativistic effects and exploration of different treatment of core correlation.

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