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Paramagnetism of closed shell diatomic hydrides with six valence electrons

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We have investigated the potential temperature independent van Vleck paramagnetism of closed shell diatomic hydrides with six valence electrons. More specifically, we have studied the magnetizability of the first row hydrides BeH^-, BH, CH^+, of the second row hydrides MgH^-, AlH, and SiH^+, and of the third row hydride GeH^+. The magnetizability was calculated using a gauge origin independent method at the uncorrelated SCF level within the random-phase approximation (RPA) as well as at different correlated levels within the second-order polarization propagator approximation (SOPPA) or various coupled cluster polarization propagator approximations (CCDPPA/CCSDPPA). We find that BH, CH^+, and SiH^+ are paramagnetic, MgH^-, AlH, and GeH^+ are diamagnetic and BeH^- is a borderline case tilting towards paramagnetism. It is primarily variations in the diamagnetic contribution to the magnetizability that determine the overall sign of the magnetizability.

I. INTRODUCTION

Lipscomb and co-workers[1] predicted in the early days of coupled Hartree–Fock theory (CHF)[2] that the simplest boron hydride molecule BH shows a temperature independent (van Vleck[3]) paramagnetism despite the fact that its electronic ground state is of $^1\Sigma^+$ symmetry. Their prediction has later been confirmed by several calculations at the uncorrelated level[4] as well as by some correlated calculations.[5–8] Hegstrom and Lipscomb[9] could also show that proofs[10,11] for the diamagnetism of closed shell molecules are valid only for systems with less than three electrons. They interpreted the paramagnetic contribution as coming from a partial unquenching of the angular momentum in the presence of the external magnetic field. The degree to which the angular momentum is unquenched depends on the separation between the ground state and excited electronic states of proper symmetry. In the case of BH with only six electrons and a low lying $^1\Pi$ state the combination of the very small diamagnetic contribution and the large paramagnetic contribution makes the total magnetizability positive.

Boucekkine–Yaker *et al.*[12] investigated later with a finite-field SCF calculation whether also the isoelectronic systems BeH^- and CH^+ show temperature independent paramagnetism. Their calculation, although being gauge origin independent because of the use of gauge including atomic orbitals (GIAO),[13] overestimated the magnetizability due to the use of a relative small basis set. They found that CH^+ would show even stronger temperature independent paramagnetism than BH, whereas BeH^- would be diamagnetic. Recently, Fowler and Steiner[14] reinvestigated this question with standard CHF theory and using larger basis sets. Their calculation is not intrinsically gauge origin independent. The size of their basis sets, however, let (with the exception of BeH^-) to only a small gauge origin dependence of the computed magnetizability.

They confirmed the paramagnetism of CH^+ and BeH^- was found to be on the borderline between para- and diamagnetism.

Laws, Stevens, and Lipscomb[15] found in their CHF study of AlH that the perpendicular component of the magnetizability is positive. However, the isotropic magnetizability was found to be slightly diamagnetic. The isoelectronic systems MgH^- and SiH^+ and the isovalent molecule GeH^+ have, to our knowledge, so far not been investigated nor have correlated calculations been reported for other molecules than BH. On the other hand, we know from the study[8] of BH, that correlation can be quite important for the magnetizability. We decided therefore to investigate: (1) if all diatomic closed shell hydrides with six valence electrons show temperature independent paramagnetism, (2) if not, where is the borderline between diamagnetism and paramagnetism. In order to obtain reliable results we used large optimized basis sets, included correlation at various levels, as well as used a gauge origin independent formulation of the magnetizability.

In the next section, a brief introduction to the calculation of magnetizabilities will be given. In Sec. III, the basis sets and computational details will be described. In Sec. IV, finally, we analyze the results for the individual molecules and the trends within the rows or columns of the periodic table.

II. THEORY

The energy E of a molecule changes due to the presence of an external homogenous magnetic field H giving rise to the magnetic flux density or induction B. The energy in the field $E(B)$ can be expanded in a Taylor series about its field free value $E(0)$

$$E(B)=E(0)+\left(\frac{\partial E}{\partial B}\right)_{B=0}\cdot B+\frac{1}{2}B\left(\frac{\partial^2 E}{\partial B\,\partial B}\right)_{B=0}B+\cdots .$$
(1)

The first derivatives of the energy with respect to the components of the magnetic induction define the components of the permanent magnetic moment m

$$m_\alpha=-\left(\frac{\partial E}{\partial B_\alpha}\right)_{B=0}$$
(2)

and the second derivatives define the components of the magnetizability tensor ξ

$$\xi_{\alpha,\beta}=-\left(\frac{\partial^2 E}{\partial B_\alpha\,\partial B_\beta}\right)_{B=0}.$$
(3)

The permanent magnetic dipole moment of a closed shell system is zero, because the orbital angular momentum is quenched and there are no unpaired spins. There will be, however, an induced magnetic moment m_{ind} in the presence of an external magnetic field

$$m_{\text{ind}}=\xi B.$$
(4)

For a closed shell system, the molecular magnetizability is the only contribution to the macroscopic magnetic susceptibility tensor χ, which relates the magnetization M to the applied magnetic field

$$M=\chi H.$$
(5)

Assuming that $\chi\ll 1$, one may write,[8]

$$\chi\approx N\mu_0\xi,$$
(6)

where N is the number density of the macroscopic sample and μ_0 is the permeability of vacuum.

Using standard second-order perturbation theory Van Vleck[3] found two contributions to the magnetizability: the so-called diamagnetic ξ^d and paramagnetic ξ^p terms

$$\xi(R)=\xi^d(R)+\xi^p(R)$$

$$=-\frac{e^2}{4m_e}\langle 0|(r-R)\cdot(r-R)1-(r-R)(r-R)|0\rangle$$

$$-\frac{e^2}{2m_e^2}\sum_{n\neq 0}\frac{\langle 0|l(R)|n\rangle\langle n|l(R)|0\rangle}{E_0-E_n}.$$
(7)

Here, R is the gauge origin, an arbitrary parameter which reflects the fact that the vector potential is not defined uniquely. Both contributions to the magnetizability show quadratic dependence on the gauge origin. Only their sum, however, has a physical meaning and must, thus, be independent of the choice of R. This is the case for exact states and for approximations like the coupled perturbed Hartree–Fock/random phase approximation (CHF/RPA) or its multiconfigurational version (MCRPA) in the limit of a complete basis set. For finite basis sets there will, however, remain a quadratic net gauge origin dependence of the total magnetizability.[8]

Geertsen[16] recently proposed a new gauge origin independent method for calculation of the trace of the magnetizability tensor. The gauge origin independence is obtained by reformulating the diamagnetic contribution as a sum-over-states so that it looks like the paramagnetic contribution[17]

$$\xi^d(R)=-\frac{e^2}{4m_e^2}\sum_{n\neq 0}\left[\frac{\langle 0|(r-R)\times l(R)+(r\times R)\times p-i\hbar r|n\rangle\langle n|p|0\rangle}{E_0-E_n}\right.$$

$$\left.+\frac{\langle 0|p|n\rangle\langle n|(r-R)\times l(R)+(r\times R)\times p-i\hbar r|0\rangle}{E_0-E_n}\right].$$
(8)

In addition to the gauge origin independence this approach has the advantages that one may use the *same* method to calculate both terms in correlated calculations of the magnetizability.

Recalling the form of the spectral representation of the polarization propagator[18] or linear response function[19]

$$\langle\langle P;Q\rangle\rangle_E=\sum_{n\neq 0}\left[\frac{\langle 0|P|n\rangle\langle n|Q|0\rangle}{E+E_0-E_n}\right.$$

$$\left.-\frac{\langle 0|Q|n\rangle\langle n|P|0\rangle}{E+E_n-E_0}\right],$$
(9)

we see that we may determine the paramagnetic [Eq. (7)] and the diamagnetic [Eq. (8)] contribution to the magnetizability as the zero-energy limit of a polarization propagator

$$\xi^p(R)=-\frac{e^2}{4m_e^2}\langle\langle l(R);l(R)\rangle\rangle_{E=0},$$
(10)

$$\xi^d(R)=-\frac{e^2}{4m_e^2}\langle\langle(r-R)\times l(R)+(r\times R)\times p$$

$$-i\hbar r;p\rangle\rangle_{E=0}.$$
(11)

The polarization propagators are calculated using a superoperator formalism of the linear response function.[18] Electron correlation is included in our calculations by means of perturbation theory. As zeroth-order reference state we use a SCF state and as perturbation the fluctuation potential. The polarization propagator is then evaluated through nth order of the fluctuation potential. In first order, we obtain the random phase approximation, which for static properties like ξ^d and ξ^p is equivalent to the coupled perturbed Hartree–Fock method. In second order, we ob-

tain the second-order polarization propagator approxima-tion (SOPPA). In addition to all contributions up to and including second-order SOPPA also includes higher-order terms some of which are summed to infinite order. The coupled cluster doubles (CCDPPA) and coupled cluster singles and doubles polarization propagator approximation (CCSDPPA)[20] differ from SOPPA by replacing the per-turbation theory correlation coefficients by coupled cluster doubles t_2 or coupled cluster singles and doubles t_1 and t_2 amplitudes. This implies that we obtain SOPPA when we use the coupled cluster amplitudes from the first iteration in CCDPPA. Although additional higher-order terms, which sum selected contributions from single and double excitations to infinite order, are included in the CCDPPA/CCSDPPA relative to SOPPA, the CC based methods are still only consistent through second order. In contrast to earlier calculations, we include now for the first time also the W_4 term in the SOPPA and CCDPPA/CCSDPPA calculations of magnetizabilities.[21]

III. BASIS SETS AND COMPUTATIONAL DETAILS

All calculations have been performed with the Odense version of the RPAC 9.0 program package,[22] in which we included the gauge origin invariant calculation of magne-tizabilities and the CCDPPA and CCSDPPA options. The atomic integrals, molecular orbital energies, and coupled cluster amplitudes were obtained from the GAUSSIAN 92 program system,[23] which we interfaced with the RPAC pro-gram.

The calculations were performed at the ground equi-librium geometry. For BH, CH$^+$, AlH, and SiH$^+$ the ex-perimental bond lengths $R_e = 1.2324$, 1.1309, 1.6478, and 1.4941 Å from Huber and Herzberg[24] were used. The bond lengths $R_e = 1.411$ and 1.857 Å for BeH$^-$ and MgH$^-$ were taken from Rosmus and Meyer.[25] However, the bond length of $R_e = 1.5576$ Å for GeH$^+$ was obtained by geom-etry optimization at the MP2 level with the initial basis set. The center of mass, calculated from the most common isotopes, was used as gauge origin and origin of the coor-dinate system. This choice influences the subdivision of ξ in its dia- and paramagnetic parts, but has of course no effect on ξ. We used five spherical d and seven spherical f func-tions.

We studied in detail the basis set dependence of the magnetizability at the various levels of approximations for all molecules. We started the basis set study with standard sp basis sets. For the first row hydrides we used van Dui-jneveldt's[26] 11s7p basis sets for boron and carbon and the 11s basis set for beryllium. The s functions with the four largest exponents were contracted to one function. The s functions with the three smallest exponents were replaced by four s functions covering nearly the same range of ex-ponents. Operationally, this was done by using the ratio of the exponents of the last two nondeleted s functions in the generation of four s functions in an even-tempered fashion. The reason for that is, that in our study of magnetic prop-erties of triply bonded systems,[27] we observed, that omit-ting the s function in the set of six Cartesian d functions had an effect on the result of the calculation. This indicated

TABLE I. Contracted atomic Gaussian type basis sets of BeH$^-$.

No.	Basis set[a]	Functions added on Be	Functions added on H
56	[9s6p3d/5s3p][b]		
58	[11s6p3d/5s3p]	s: 0.010 998, 0.004 388	
62	[11s6p3d/9s3p]		s: 0.030 085, 0.011 330, 0.004 266, 0.001 607
77	[11s6p3d/9s8p]		p: 0.101 747, 0.035 454, 0.012 354, 0.004 305, 0.001 500
82	[11s6p4d/9s8p]	d: 1.863 600	
87	[11s6p4d/9s8p1d]		d: 0.006 616
94	[11s6p4d1f/9s8p1d]	f: 0.111 070	
101	[11s6p4d2f/9s8p1d]	f: 0.027 108	
108	[11s6p4d3f/9s8p1d]	f: 0.006 616	
115	[11s6p4d4f/9s8p1d]	f: 0.455 090	

[a]The functions listed in front of the solidus are centered on the heavy atom, whereas the functions listed after the solidus are centered on the hydrogen atom.
[b]van Duijneveldt[26] 11s basis set for beryllium and 7s basis set for hydro-gen. The s functions with the three smallest exponents for beryllium were replaced by four s functions with exponents $\zeta_s = 0.434112$, 0.173 194, 0.069 098, 0.027 567. The s functions with the four largest exponents for beryllium and the three largest exponents for hydrogen were contracted. Six p functions and three d functions with exponents $\zeta_d = 0.455090$, 0.111 070, 0.027 108 from Sadlej and Urban (Ref. 29) were added for beryllium and the 3p basis set from Dunning (Ref. 28) was added for hydrogen.

that there is a gap in the series of exponents for the s functions in van Duijneveldt's energy optimized basis sets, which is important for calculation of magnetic properties. We decided, therefore, to replace the diffuse part of the s-basis set by an even-tempered series and to use spherical d and f functions. For boron and carbon we used the 3d and the 1f or 2f set of polarization and second polariza-

TABLE II. Contracted atomic Gaussian type basis sets of BH.

No.	Basis set[a]	Functions added on B	Functions added on H
59	[9s7p3d/5s3p][b]		
62	[9s8p3d/5s3p]	p: 0.020 688	
63	[9s8p3d/6s3p]		s: 0.030 085
73	[9s8p5d/6s3p]	d: 3.064 925, 0.052 301	
79	[9s8p5d/6s5p]		p: 0.101 747, 0.035 454
86	[9s8p5d1f/6s5p]	f: 0.490[c]	
93	[9s8p5d2f/6s5p]	f: 0.490 replaced by 0.882, 0.311[c]	
98	[9s8p5d2f/6s5p1d]		d: 1.057[d]
105	[9s8p5d3f/6s5p1d]	f: 0.124 219	
110	[9s8p5d3f/6s5p2d]		d: 1.057 replaced by 2.062, 0.662[d]

[a]See footnote a of Table I.
[b]van Duijneveldt[26] 11s7p basis set for boron and 7s basis set for hydrogen. The s functions with the three smallest exponents for boron were replaced by four s functions with exponents $\zeta_s = 0.696162$, 0.280 732, 0.113 207, 0.045 652. The s functions with the four largest exponents for boron and the three largest exponents for hydrogen were contracted. Dunning (Ref. 28) 3d basis set for boron and 3p basis set for hydrogen were added.
[c]Dunning's (Ref. 28) 1f and 2f basis sets for boron.
[d]Dunning's (Ref. 28) 1d and 2d basis sets for hydrogen.

TABLE III. Contracted atomic gaussian type basis sets of CH^+.

No.	Basis set[a]	Functions added on C	Functions added on H
59	$[9s7p3d/5s3p]^b$		
74	$[9s7p6d/5s3p]$	d: 14.984, 5.262, 0.080	
77	$[9s7p6d/5s4p]$		p: 0.101 747
84	$[9s7p6d1f/5s4p]$	f: 0.761[c]	
91	$[9s7p6d2f/5s4p]$	f: 0.761 replaced by 1.419, 0.485[c]	
96	$[9s7p6d2f/5s4p1d]$		d: 1.057[d]
103	$[9s7p6d3f/5s4p1d]$	f: 0.165 768	
108	$[9s7p6d3f/5s4p2d]$		d: 1.057 replaced by 2.062, 0.662[d]

[a]See footnote a of Table I.
[b]van Duijneveldt (Ref. 26) $11s7p$ basis set for carbon and $7s$ basis set for hydrogen. The s functions with the three smallest exponents for carbon were replaced by four s functions with exponents ζ_s = 1.092 350, 0.437 465, 0.175 196, 0.070 163. The s functions with the four largest exponents for carbon and the three largest exponents for hydrogen were contracted. Dunning (Ref. 28) $3d$ basis set for carbon and $3p$ basis set for hydrogen were added.
[c]Dunning's (Ref. 28) $1f$ and $2f$ basis sets for carbon.
[d]Dunning's (Ref. 28) $1d$ and $2d$ basis sets for hydrogen.

tion functions, respectively, from Dunning.[28] The p, d, and f functions for beryllium were taken from Sadlej and Urban.[29]

For the second row atoms, we used the uncontracted $11s7p$ basis sets from the recent basis set optimization study by Schäfer, Horn, and Ahlrichs[30] as our initial basis

TABLE IV. Contracted atomic Gaussian type basis sets of MgH^-.

No.	Basis set[a]	Functions added on Mg	Functions added on H
62	$[9s8p3d/5s3p]^b$		
64	$[11s8p3d/5s3p]$	s: 0.013 526 578 548, 0.005 105 888 9821	
68	$[11s8p3d/9s3p]$		s: 0.030 085, 0.011 330, 0.004 266, 0.001 607
78	$[11s8p5d/9s3p]$	d: 2.769 529 609 6, 0.034 246 123 669	
93	$[11s8p5d/9s8p]$		p: 0.101 747, 0.035 454, 0.012 354, 0.004 305, 0.001 500
100	$[11s8p5d1f/9s8p]$	f: 0.102 697 546 61	
107	$[11s8p5d2f/9s8p]$	f: 0.034 246 123 669	
112	$[11s8p5d2f/9s8p1d]$		d: 0.006 616
119	$[11s8p5d3f/9s8p1d]$	f: 0.307 970 215 30	

[a]See footnote a of Table I.
[b]The $11s7p$ basis set for magnesium from Schäfer, Horn, and Ahlrichs (Ref. 30) and the van Duijneveldt (Ref. 26) $7s$ basis set for hydrogen. The s functions with the four smallest exponents for magnesium were replaced by six s functions with exponents ζ_s = 4.676 140 036, 1.765 106 5005, 0.666 276 235 42, 0.251 499 851 01, 0.094 933 860 308, 0.035 834 764 103, the p functions with the two smallest exponents for magnesium were replaced by three functions with exponents ζ_p = 0.307 970 215 30, 0.102 697 546 61, 0.034 246 123 669. The s functions with the five largest exponents for magnesium and the three largest exponents for hydrogen were contracted. Dunning's (Ref. 28) $3p$ basis set for hydrogen and three d functions for magnesium with exponents ζ_d = 0.923 543 518 28, 0.307 970 215 30, 0.102 697 546 61 were added.

TABLE V. Contracted atomic Gaussian type basis sets of AlH.

No.	Basis set[a]	Functions added on Al	Functions added on H
59	$[9s7p3d/5s3p]^b$		
62	$[9s8p3d/5s3p]$	p: 0.016 246 041	
63	$[9s8p3d/6s3p]$		s: 0.030 085
78	$[9s8p6d/6s3p]$	d: 10.374 524, 0.139 611 94, 0.047 625 008	
87	$[9s8p6d/6s6p]$		p: 0.101 747, 0.035 454, 0.012 354
94	$[9s8p6d1f/6s6p]$	f: 0.409 270 17	
101	$[9s8p6d2f/6s6p]$	f: 0.139 611 94	
106	$[9s8p6d2f/6s6p1d]$		d: 1.057[c]
113	$[9s8p6d3f/6s6p1d]$	f: 1.199 7689	
118	$[9s8p6d3f/6s6p2d]$		d: 1.057 replaced by 2.062, 0.662[c]

[a]See footnote a of Table I.
[b]The $11s7p$ basis set for aluminum from Schäfer, Horn, and Ahlrichs (Ref. 30) and the van Duijneveldt (Ref. 26) $7s$ basis set for hydrogen. The s functions with the four smallest exponents for aluminum were replaced by six s functions with exponents ζ_s = 5.618 9559, 2.120 9992, 0.800 618 04, 0.302 210 99, 0.114 076 22, 0.043 060 591, the p functions with the two smallest exponents for aluminum were replaced by three functions with exponents ζ_p = 0.409 270 17, 0.139 611 94, 0.047 625 008. The s functions with the five largest exponents for aluminum and the three largest exponents for hydrogen were contracted. Dunning's (Ref. 28) basis set for hydrogen and three d functions for aluminum with exponents ζ_d = 3.517 1032, 1.199 7689, 0.409 270 17 were added.
[c]Dunning's (Ref. 28) $1d$ and $2d$ basis sets for hydrogen.

set. The s functions with the five largest exponents were contracted, the s functions with the four smallest exponents and p functions with the two smallest exponents were replaced by even tempered series of six s functions and three p functions. The exponents for the d and f functions were set equal to some of the exponents for the p functions (see Tables IV–VI). For germanium, we used the $(14s11p5d)$ contracted to $[8s6p2d]$ basis set from Schäfer, Horn, and Ahlrichs.[30] Again, we replaced the s functions with the four smallest exponents, the p functions with the three smallest exponents and the d functions with the smallest exponent with an even tempered series of $6s$, $4p$, and $4d$ functions. Three f functions with exponents equal to those of the d functions were added. For hydrogen we used the $7s$ basis set from van Duijneveldt[26] contracted to $5s$ and the $3p$ and $1d$ or $2d$ polarization functions from Dunning[28] for all molecules with the exception of BeH^- and MgH^- where only one d function with a much smaller exponent was added.

The basis sets described above were systematically improved by adding more functions by continuing the even-tempered series until the change in the magnetizability was negligible. Summaries of the added functions, that had an effect on the magnetizability, are given in Tables I–VII. Table VIII gives total energies and Thomas–Reiche–Kuhn (TRK) sum rules for all hydrides. In a complete basis set RPA calculation the TRK sum rule is equal to the number of electrons. The total SCF energies for the first row hydrides are lower than the SCF energies of Fowler and Steiner[14] and Rosmus and Meyer,[25] because we use larger basis sets. In our previous study of BH,[8] however, the SCF

TABLE VI. Contracted atomic Gaussian type basis sets of SiH$^+$.

No.	Basis set[a]	Functions added on Si	Functions added on H
59	[9s7p3d/5s3p][b]		
74	[9s7p6d/5s3p]	d: 12.741 923, 0.184 247 05, 0.064 166 149	
77	[9s7p6d/5s4p]		p: 0.101 747
84	[9s7p6d1f/5s4p]	f: 0.529 048 04	
91	[9s7p6d2 f/5s4p]	f: 0.184 247 05	
96	[9s7p6d2 f/5s4p1d]		d: 1.057[c]
103	[9s7p6d3f/5s4p1d]	f: 1.519 1116	
108	[9s7p6d3 f/5s4p2d]		d: 1.057 replaced by 2.062, 0.662[c]

[a]See footnote a of Table I.
[b]The 11s7p basis set for silicon from Schäfer, Horn, and Ahlrichs (Ref. 30) and the van Duijneveldt (Ref. 26) 7s basis set for hydrogen. The s functions with the four smallest exponents for silicon were replaced by six s functions with exponents ζ_s=6.662 4892, 2.513 9455, 0.948 582 67, 0.357 927 05, 0.135 055 99, 0.050 960 441, the p functions with the two smallest exponents for silicon were replaced by three functions with exponents ζ_p=0.529 048 04, 0.184 247 05, 0.064 166 149. The s functions with the five largest exponents for silicon and the three largest exponents for hydrogen were contracted. Dunning's (Ref. 28) 3p basis set for hydrogen and three d functions for silicon with exponents ζ_d=4.361 9858, 1.519 1116, 0.529 048 04 were added.
[c]Dunning's (Ref. 28) 1d and 2d basis sets for hydrogen.

TABLE VII. Contracted atomic Gaussian type basis sets of GeH$^+$.

No.	Basis set[a]	Functions added on Ge	Functions added on H
104	[10s7p5d3f/5s4p2d][b]	f: 0.896 368 818, 0.313 092 884, 0.109 360 290	p: 0.101 747 d: 2.062, 0.662[c]
109	[10s7p6d3 f/5s4p2d]	d: partially uncontracted[d]	
116	[10s7p6d4 f/5s4p2d]	f: 2.566 257 8101	
123	[10s7p6d5 f/5s4p2d]	f: 7.347 064 0817	
130	[10s7p6d6 f/5s4p2d]	f: 21.313 162 441	
140	[10s7p8d6 f/5s4p2d]	d: totally uncontracted[e]	

[a]See footnote a of Table I.
[b][14s11p5d] from Schäfer, Horn, and Ahlrichs (Ref. 30) contracted to [8s6p2d] for germanium and van Duijneveldt (Ref. 26) 7s basis set for hydrogen. The s functions with the four smallest exponents for germanium were replaced by six s functions with exponents ζ_s =5.300 389 8720, 2.198 410 226, 0.965 848 390, 0.424 335 322, 0.186 427 257, 0.081 904 853, the p functions with the three smallest exponents for germanium were replaced by four functions with exponents ζ_p=1.233 984 641, 0.513 772 785, 0.213 910 664, 0.089 062 274 and the d function with the smallest exponent for germanium was replaced by four functions with exponents ζ_d=0.896 368 818, 0.313 092 884, 0.109 360 290, 0.038 198 482. The s functions with the three largest exponents for hydrogen were contracted. Dunning's (Ref. 28) 3p basis set for hydrogen was added.
[c]Dunning's (Ref. 28) 2d basis set for hydrogen.
[d]The d-function with exponent ζ_d=2.566 257 8101 was removed from the contraction of basis set 104 and added as uncontracted function.
[e]The d-functions with exponents ζ_d=74.790 227 510, 21.313 162 441 were removed from the contraction of basis set 130 and added as uncontracted functions.

TABLE VIII. Energies and Thomas–Reiche–Kuhn sum rule.[a]

	E_{SCF}	Δ_{MP2}	Δ_{CCD}	$S^L_{RPA}(0)$
BeH$^-$	−15.134 369	−0.098 487	−0.120 212	5.9792
BH	−25.130 131	−0.120 825	−0.145 878	5.9977
CH$^+$	−37.909 474	−0.138 106	−0.166 508	5.9978
MgH$^-$	−200.142 216	−0.323 205	−0.341 655	13.5588
AlH	−242.447 136	−0.379 097	−0.379 557	13.9086
SiH$^+$	−289.147 803	−0.393 182	−0.412 867	13.9175
GeH$^+$	−2075.566 951	−1.191 957		29.9230

[a]E_{SCF} is the Hartree–Fock SCF total energy, Δ_{MP2} and Δ_{CCD} are the MP2 and coupled cluster doubles correlation energies, $S^L_{RPA}(0)$ is the RPA value of the Thomas–Reiche–Kuhn sum rule in the length representation. All are expressed in atomic units: 1 a.u. of $E=E_h\approx4.35975\times10^{-18}$ J. The largest basis sets in Tables I–VII are used.

total energy was even lower and the CCSD correlation energy slightly smaller. The fulfillment of the TRK sum rule $S^L_{RPA}(0)$ is perfect for all three first row molecules. For the second row hydrides, our total SCF energies are slightly higher than those of Rosmus and Meyer,[25] but the TRK sum rule is, with the exception of MgH$^-$, still very good. The fulfillment of the TRK for GeH$^+$ is acceptable.

The results for the magnetizability at the various levels of approximation as a function of the basis sets are given in Tables IX–XV. The magnetizabilities at the SOPPA, CCDPPA, and CCSDPPA level show a parallel dependence on the basis set for all systems studied, which differs, however, from the one observed at the RPA level. We do not see any effect of second polarization functions at the RPA level, but only at the correlated level. As pointed out earlier,[8] it is thus not possible to determine a converged basis set to be used in a correlated calculation by optimizing the basis set at the uncorrelated level. We believe, that the basis sets are converged for all systems at the RPA level, and that the magnetizabilities reported are close to the RPA/SCF limit. We did not test the importance of the next level of polarization functions, but based on the effect of the second polarization functions we believe it to be small. Therefore, the correlated results for the magnetizabilities are also expected to be close to the basis set limits. The basis set of GeH$^+$, however, is not of the same quality, as Ge has occupied d orbitals and a comparable basis set should include g functions. On the other hand, from the experience with the first and second row systems we do not expect g functions to change the result fundamentally.

IV. RESULTS AND DISCUSSION

Table XVI compares the magnetizabilities in the largest basis sets with earlier uncorrelated and correlated calculations. We have given an estimate of the CCSDPPA results for the basis sets, for which we could not obtain CCSD t_1 and t_2 amplitudes from the GAUSSIAN 92 program, based on the parallel basis set dependence of the CCDPPA and CCSDPPA results found for smaller basis sets. From our calculation, we can safely say that BH, CH$^+$, and SiH$^+$ are paramagnetic whereas MgH$^-$ is diamagnetic. Even though BeH$^-$, AlH, and GeH$^+$ all have small magnetizabilities, we believe that our calculations can be

TABLE IX. Gauge origin independent magnetizability ξ of BeH^- as a function of level of approximation and basis set size.[a]

No.	ξ^d				ξ^p				ξ			
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA
56	−9.3955	−9.0761	−8.6759	−8.4463	10.9089	11.3364	9.7626	9.4915	1.5134	2.2604	1.0867	1.0452
58	−9.5676	−9.3846	−8.9225	−8.6778	10.1055	10.6434	9.2976	9.1206	0.5379	1.2589	0.3751	0.4429
62	−9.7021	−9.5509	−9.0635	−8.8159	10.1019	10.6432	9.3002	9.1238	0.3998	1.0923	0.2367	0.3079
77	−10.1566	−10.0952	−9.5449	−9.2774	10.1552	10.7207	9.3870	9.2221	−0.0014	0.6255	−0.1580	−0.0553
82	−10.1574	−10.0702	−9.5287	−9.2573	10.1498	10.7153	9.3911	9.2200	−0.0076	0.6451	−0.1376	−0.0373
87	−10.1738	−10.0914	−9.5417	−9.2668	10.1515	10.7191	9.3951	9.2240	−0.0223	0.6278	−0.1466	−0.0428
94	−10.1813	−10.1925	−9.7616	−9.4917	10.1538	10.9175	9.6759	9.5064	−0.0275	0.7250	−0.0857	0.0148
101	−10.1849	−10.2560	−9.8277	−9.5513	10.1582	10.9461	9.7047	9.5335	−0.0267	0.6900	−0.1231	−0.0178
108	−10.1882	−10.2636	−9.8351		10.1586	10.9470	9.7057		−0.0296	0.6834	−0.1294	
115	−10.1884	−10.1851	−9.8277		10.1598	10.9503	9.8061		−0.0286	0.7653	−0.0216	

[a]ξ^d, ξ^p, and ξ are the diamagnetic, paramagnetic, and total magnetizability, respectively. Atomic units are used: 1 a.u. of $\xi = e^2 a_0^2 m_e^{-1} \approx 7.891\,04 \times 10^{-29}$ JT^{-2}.

TABLE X. Gauge origin independent magnetizability ξ of BH as a function of level of approximation and basis set size. (See footnote of Table IX.)

No.	ξ^d				ξ^p				ξ			
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA
59	−3.5697	−3.5272	−3.5265	−3.4946	7.6120	7.8026	6.7239	6.6279	4.0424	4.2754	3.1974	3.1334
62	−3.5717	−3.5292	−3.5284	−3.4965	7.6119	7.8024	6.7240	6.6281	4.0402	4.2732	3.1956	3.1316
63	−3.5763	−3.5334	−3.5323	−3.5000	7.6109	7.8014	6.7234	6.6275	4.0347	4.2680	3.1911	3.1275
73	−3.7031	−3.6507	−3.6443	−3.6075	7.6310	7.8401	6.7581	6.6625	3.9279	4.1893	3.1139	3.0549
79	−3.7399	−3.6908	−3.6843	−3.6496	7.6414	7.8524	6.7711	6.6760	3.9015	4.1616	3.0868	3.0264
86	−3.7439	−3.7211	−3.7310	−3.6961	7.6437	8.0216	6.9761	6.8795	3.8998	4.3005	3.2451	3.1834
93	−3.7446	−3.7312	−3.7475	−3.7126	7.6445	8.0566	7.0306	6.9329	3.8999	4.3254	3.2831	3.2204
98	−3.7448	−3.7360	−3.7549	−3.7197	7.6475	8.0443	7.0346	6.9371	3.9027	4.3083	3.2797	3.2174
105	−3.7455	−3.7430	−3.7641	−3.7287	7.6475	8.0522	7.0438	6.9463	3.9021	4.3092	3.2797	3.2175
110	−3.7454	−3.7460	−3.7682		7.6476	8.0548	7.0511		3.9022	4.3088	3.2829	

TABLE XI. Gauge origin independent magnetizability ξ of CH^+ as a function of level of approximation and basis set size. (See footnote of Table IX.)

No.	ξ^d				ξ^p				ξ			
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA
59	−2.1310	−2.1193	−2.1267	−2.1155	8.7007	8.5410	6.7638	6.6714	6.5697	6.4217	4.6371	4.5559
74	−2.1522	−2.1382	−2.1450	−2.1333	8.6993	8.5722	6.7902	6.6970	6.5471	6.4340	4.6451	4.5637
77	−2.1543	−2.1404	−2.1472	−2.1356	8.7001	8.5733	6.7911	6.6980	6.5458	6.4329	4.6439	4.5624
84	−2.1587	−2.1591	−2.1472	−2.1606	8.7044	8.7976	7.0059	6.9146	6.5457	6.6385	4.8335	4.7540
91	−2.1593	−2.1628	−2.1784	−2.1665	8.7063	8.8431	7.0659	6.9733	6.5471	6.6803	4.8875	4.8068
96	−2.1594	−2.1658	−2.1824	−2.1705	8.7132	8.8233	7.0620	6.9702	6.5539	6.6576	4.8797	4.7997
103	−2.1598	−2.1676	−2.1846	−2.1728	8.7132	8.8270	7.0657	6.9738	6.5534	6.6594	4.8811	4.8011
108	−2.1597	−2.1685	−2.1858		8.7130	8.8210	7.0657		6.5533	6.6525	4.8799	

TABLE XII. Gauge origin independent magnetizability ξ of MgH^- as a function of level of approximation and basis set size. (See footnote of Table IX.)

No.	ξ^d				ξ^p				ξ			
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA
62	−9.7407	−9.4050	−9.2665	−9.1643	9.4287	9.3964	8.6779	8.4864	−0.3120	−0.0085	−0.5886	−0.6779
64	−9.4073	−9.1657	−9.0801	−9.0249	8.8206	8.9149	8.3024	8.2034	−0.5867	−0.2509	−0.7777	−0.8215
68	−9.7272	−9.4136	−9.2953	−9.2060	8.7393	8.8272	8.2508	8.1337	−0.9879	−0.5864	−1.0445	−1.0723
78	−11.7391	−11.2800	−11.1420	−11.0097	9.0525	9.2575	8.6988	8.6072	−2.6866	−2.0226	−2.4432	−2.4025
93	−13.1617	−12.5841	−12.3617	−12.1096	10.0702	10.1349	9.4296	9.2636	−3.0915	−2.4492	−2.9320	−2.8460
100	−13.1749	−12.7901	−12.7071	−12.4553	10.0764	10.3221	9.7058	9.5318	−3.0985	−2.4679	−3.0013	−2.9235
107	−13.1899	−12.8681	−12.8081	−12.5519	10.0771	10.3466	9.7358	9.5606	−3.1128	−2.5215	−3.0723	−2.9913
112	−13.9649	−13.4543	−13.3164		10.1323	10.3951	9.7769		−3.8326	−3.0592	−3.5394	
119	−13.9719	−13.4219	−13.3287		10.1383	10.3887	9.8170		−3.8337	−3.0332	−3.5117	

TABLE XIII. Gauge origin independent magnetizability ξ of AlH as a function of level of approximation and basis set size. (See footnote of Table IX.)

No.	ξ^d				ξ^p				ξ			
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA
59	−5.6664	−5.4941	−5.4308	−5.3923	6.4632	6.3516	5.9239	5.8376	0.7968	0.8575	0.4931	0.4453
62	−5.6718	−5.4992	−5.4359	−5.3975	6.4638	6.3522	5.9247	5.8386	0.7921	0.8529	0.4888	0.4411
63	−5.6842	−5.5106	−5.4469	−5.4080	6.4640	6.3524	5.9250	5.8390	0.7798	0.8417	0.4782	0.4310
78	−6.9374	−6.7523	−6.7121	−6.6521	6.8362	6.9644	6.5341	6.4644	−0.1013	0.2120	−0.1780	−0.1877
87	−7.1405	−6.9585	−6.9160	−6.8552	6.9119	7.0416	6.6116	6.5410	−0.2286	0.0832	−0.3045	−0.3143
94	−7.1627	−7.0232	−7.0105	−6.9481	6.9251	7.1414	6.7474	6.6727	−0.2376	0.1182	−0.2631	−0.2754
101	−7.1713	−7.0940	−7.1044	−7.0416	6.9275	7.2065	6.8294	6.7541	−0.2438	0.1125	−0.2749	−0.2875
106	−7.1717	−7.1074	−7.1264	−7.0633	6.9312	7.1969	6.8405	6.7650	−0.2406	0.0895	−0.2859	−0.2983
113	−7.1719	−7.1055	−7.1257		6.9289	7.1944	6.8421		−0.2429	0.0889	−0.2836	
118	−7.1723	−7.1163	−7.1411		6.9305	7.2029	6.8579		−0.2417	0.0866	−0.2833	

TABLE XIV. Gauge origin independent magnetizability ξ of SiH$^+$ as a function of level of approximation and basis set size. (See footnote of Table IX.)

No.	ξ^d				ξ^p				ξ			
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA	RPA	SOPPA	CCDPPA	CCSDPPA
59	−4.1762	−4.0892	−4.0648	−4.0471	5.8555	5.8521	5.4152	5.3602	1.6793	1.7629	1.3504	1.3131
74	−4.7409	−4.6481	−4.4347	−4.4045	6.0173	6.1826	5.4514	5.4029	1.2765	1.5345	1.0168	0.9984
77	−4.7792	−4.6858	−4.6735	−4.6446	6.0313	6.1967	5.7565	5.7073	1.2521	1.5109	1.0830	1.0628
84	−4.8074	−4.7499	−4.7551	−4.7249	6.0436	6.3163	5.9053	5.8543	1.2363	1.5664	1.1502	1.1294
91	−4.8190	−4.7890	−4.8030	−4.7723	6.0469	6.3585	5.9552	5.9038	1.2279	1.5694	1.1522	1.1315
96	−4.8202	−4.8002	−4.8183	−4.7878	6.0525	6.3434	5.9543	5.9037	1.2324	1.5432	1.1359	1.1158
103	−4.8205	−4.8001	−4.8189	−4.7882	6.0491	6.3442	5.9594	5.9080	1.2286	1.5441	1.1406	1.1199
108	−4.8209	−4.8062	−4.8270		6.0500	6.3479	5.9670		1.2291	1.5417	1.1400	

TABLE XV. Gauge origin independent magnetizability ξ of GeH$^+$ as a function of level of approximation and basis set size. (See footnote of Table IX.)

No.	ξ^d			ξ^p			ξ		
	RPA	SOPPA	CCDPPA	RPA	SOPPA	CCDPPA	RPA	SOPPA	CCDPPA
104	−5.5652	−5.6170	−5.6450	6.0981	6.4097	6.1017	0.5330	0.7927	0.4567
109	−5.6437	−5.6860	−5.7187	6.1028	6.4158	6.1318	0.4591	0.7298	0.4131
116	−6.2387	−6.2347	−6.2757	6.1015	6.4343	6.2064	−0.1372	0.1996	−0.0693
123	−6.3990	−6.3800		6.1040	6.4400		−0.2949	0.0600	
130	−6.4128	−6.3916		6.1043	6.4405		−0.3085	0.0488	
140	−6.4329	−6.4079		6.1084	6.4497		−0.3245	0.0418	

TABLE XVI. Comparison of the magnetizability with earlier calculations.[a]

	This work[b]				Other	
	RPA	SOPPA	CCDPPA	CCSDPPA	RPA/CHF	Correlated
BeH$^-$	−0.029	0.765	−0.022	0.08[c]	−0.077[d]	
BH	3.902	4.309	3.283	3.22[c]	3.891[d]	2.08[e]
CH$^+$	6.553	6.653	4.880	4.80[c]	6.548[d]	
MgH$^-$	−3.83	−3.033	−3.512	−3.43[c]		
AlH	−0.242	0.087	−0.283	−0.30[c]	−0.29[f]	
SiH$^+$	1.229	1.542	1.140	1.12[c]		
GeH$^+$	−0.325	0.042	<0[c]	<0[c]		

[a] Atomic units are used: 1 a.u. of $\xi = e^2 a_0^2 m_e^{-1} \approx 7.89104 \times 10^{-29}$ JT^{-2}.
[b] Basis set 115 for BeH$^-$, 110 for BH, 108 for CH$^+$, 119 for MgH$^-$, 118 for AlH, 108 for SiH$^+$, and 140 for GeH$^+$.
[c] Estimated values based on the almost constant difference between the CCDPPA and CCSDPPA results for smaller basis sets (see the text).
[d] Reference 14.
[e] Reference 7.
[f] Reference 15.

TABLE XVII. Electronic spatial extent $\langle r^2 \rangle$ (in a.u.) calculated from the SCF density.

	Basis set	$\langle r^2 \rangle$
BeH^-	115	61.2648
BH	110	22.4797
CH^+	108	12.9651
MgH^-	119	85.0545
AlH	118	43.0859
SiH^+	108	28.9751
GeH^+	140	38.6502

trusted to predict AlH and GeH^+ to being diamagnetic. In the case of GeH^+, it was only possible to perform coupled cluster calculations for the smaller basis sets. We therefore cannot give a final result for it at the highest level of approximation. Nevertheless, we expect GeH^+ to be diamagnetic at the CCDPPA level based on the trends of the RPA results as a function of the basis sets as well as the comparison with the few available CCDPPA results. As for BeH^-, the situation is still not settled. We find it to be slightly paramagnetic at the highest level of theory. Hence, the borderline between dia- and paramagnetism goes through BeH^-, between AlH and SiH^+ and between SiH^+ and GeH^+ and we can order the molecules according to increasing paramagnetism as

$$\xi(MgH^-) < \xi(GeH^+) \approx \xi(AlH) < 0 \approx \xi(BeH^-)$$

$$< \xi(SiH^+) < \xi(BH) < \xi(CH^+).$$

Only for the first row hydrides and AlH, it is possible to compare with earlier calculations. Our RPA results for the first row hydrides are slightly more positive than those of Fowler and Steiner[14] making BH and CH^+ more paramagnetic and BeH^- less diamagnetic. We expect our result for BeH^- to be more reliable, because Fowler and Steiner used the same type of basis set for all three systems, whereas we optimized the basis set for each molecule indi-

vidually. We also obtain a slightly less diamagnetic result for AlH at the RPA level than Laws, Stevens, and Lipscomb[15] again most likely due to basis set differences. The recent MC–IGLO calculation[7] of the magnetizability of BH, as well as the earlier results in Refs. 5 and 6, give a much smaller value. We believe, as discussed in our study of BH,[8] that this is a consequence of the lack of dynamic correlation in the multiconfigurational approaches.

In order to understand the different results for the first, second and third row hydrides as well as the trend when going from the anions to the cations, it is useful to analyze the individual contributions to the magnetizabilities. We can see from Tables IX–XV, that the change in the magnetizability is dominated by the change in the diamagnetic contribution. This is the case within the rows as well as between the rows.

The diamagnetic contribution is essentially determined be the spatial extent or average size of the electron cloud (Table XVII). It increases within the rows from the positively charged to the negatively charged molecules and from the first to the third row. With the exception of AlH and BeH^- the order of the diamagnetic term determines the order of the total magnetizability. The size of the electron cloud, therefore, decides where the borderline between temperature independent paramagnetism and diamagnetism lies.

For the neutral and positively charged molecules the changes in the paramagnetic contribution can be understood from the fact that the lowest excitation contributes between 77% (AlH) and 97% (CH^+) (Tables XVII–XX) to the paramagnetic term at the RPA level. This excitation is mainly an HOMO–LUMO excitation between the lone pair on the heavy atom and the low lying π orbital. Its small excitation energy (between 2.64 eV for CH^+ and 3.51 eV for SiH^+ at the RPA level) and the fact that it has the largest magnetic dipole transition moment of all excitations explain the large paramagnetic contribution from this state alone. The dependence of the paramagnetic con-

TABLE XVIII. Contribution to the paramagnetic magnetizability ξ^p of BeH^-, BH, and CH^+ from individual excitations at the RPA level.[a]

n	BeH^{-b}			BH^c			CH^{+d}		
	ΔE_n	$\|\langle 0\|l_\perp\|n \rangle\|$	% of ξ^P	ΔE_n	$\|\langle 0\|l_\perp\|n \rangle\|$	% of ξ^P	ΔE_n	$\|\langle 0\|l_\perp\|n \rangle\|$	% of ξ^P
1	0.65	0.0900	1.12	2.65	1.4423	93.01	2.64	1.5729	97.40
2	0.86	0.2962	10.23	7.42	0.1196	93.24	14.66	0.3252	98.15
3	1.18	0.0868	10.80	8.55	0.0752	93.32	16.79	0.1381	98.27
4	1.25	0.6561	41.65	10.33	0.1346	93.52	18.11	0.2162	98.53
5	1.36	0.0353	41.73	11.15	0.4077	95.29	22.80	0.1844	98.69
6	1.82	0.8504	77.24	11.54	0.2460	95.91	26.46	0.0961	98.73
7	2.73	0.5418	86.83	13.97	0.3072	96.71	27.92	0.1230	98.78
8	3.37	0.1929	87.82	15.53	0.0782	96.76	28.52	0.2648	99.04
9	4.03	0.0228	87.73	16.42	0.1382	96.90	30.84	0.0020	99.04
10	5.17	0.3364	89.78	18.66	0.0629	96.92	32.69	0.0206	99.04

[a]ΔE_n is the excitation energy to the nth state of proper symmetry, $\|\langle 0\|l_\perp\|n \rangle\|$ the perpendicular component of the magnetic dipole transition moment, % of ξ^P the percentage of the paramagnetic term, one obtains by performing the sum in Eq. (7) up to and including n. Atomic units are used if not specified otherwise: 1 a.u. of $\langle 0\|l\|n \rangle = h \approx 1.05457 \times 10^{-34}$ Js.
[b]For basis set 115.
[c]For basis set 110.
[d]For basis set 108.

TABLE XIX. Contribution to the paramagnetic magnetizability ξ^P of MgH^-, AlH, and SiH^+ from individual excitations at the RPA level. (See footnote a of Table XVIII.)

	MgH$^{-\,a}$			AlH$^{\,b}$			SiH$^{+\,c}$		
n	ΔE_n	$|\langle 0|l_\perp|n\rangle|$	% of ξ^P	ΔE_n	$|\langle 0|l_\perp|n\rangle|$	% of ξ^P	ΔE_n	$|\langle 0|l_\perp|n\rangle|$	% of ξ^P
1	0.79	0.1052	1.25	2.99	1.3290	77.25	3.51	1.4241	86.52
2	1.05	0.4128	15.71	6.13	0.2831	78.96	11.16	0.1069	86.68
3	1.34	0.1773	17.81	6.45	0.2456	80.19	11.76	0.6076	91.38
4	1.66	0.8422	56.03	7.75	0.1424	80.53	13.42	0.0130	91.39
5	2.74	0.7120	72.57	8.56	0.4917	84.22	16.78	0.5527	94.11
6	3.85	0.3156	74.88	8.74	0.1969	84.80	18.05	0.1708	94.36
7	4.68	0.2243	75.84	10.73	0.4215	86.97	18.87	0.3001	95.07
8	5.54	0.3466	77.79	11.60	0.0785	87.04	20.60	0.1796	95.31
9	5.78	0.2226	78.55	12.13	0.4161	88.91	23.72	0.3063	95.90
10	5.89	0.2239	79.32	12.50	0.3912	90.51	25.18	0.2531	96.28

[a]For basis set 119.
[b]For basis set 118.
[c]For basis set 108.

tribution on the level of approximation as well as its variation from one molecule to the other thus come from changes in this excitation energy (Table XXI). It increases from left to right within the rows and from the first to the second row. The excitation energy of GeH$^+$ is slightly lower than the one of SiH$^+$. Based on our experience from the basis set study on the other systems, we expect second polarization functions on Ge to decrease the excitation energy even further. SOPPA always gives too small excitation energies for molecules of the kind discussed here whereas we obtain rather good agreement with experimental data (when available) at the CCSDPPA level. We believe, therefore, that the paramagnetic contributions at the CCSDPPA are rather accurate.

In case of the anions the lowest $^1\Pi \leftarrow {}^1\Sigma^+$ excitation gives a contribution of only about 1% despite the low excitation energies (see Table XXI). In fact, there is an even lower excitation of $^1\Sigma^+ \leftarrow {}^1\Sigma^+$ symmetry, that does not contribute to the paramagnetic term. All excitations below 4 eV, however, give again between 75% (MgH$^-$ with six excitations) and 88% (BeH$^-$ with nine excitations) like for the other systems. The large number of very low-lying excited states and the fact that the magnetic dipole transition moments are much more equally distributed over

them makes this understandable. Overall ξ^P of the anions is larger than for the other systems and there is only a small difference between BeH$^-$ and MgH$^-$. However, all these differences are small compared to the differences in ξ^d as discussed above.

V. CONCLUSION

We have investigated, whether the well-documented temperature independent paramagnetism of BH also holds for other closed shell diatomic hydrides with six valence electrons and a $^1\Sigma^+$ ground state. A gauge origin independent method was used to calculate the magnetizability at the uncorrelated RPA level as well as at the correlated SOPPA, CCDPPA, and CCSDPPA levels. An extended basis set study was made in order to obtain results, which are converged also at the correlated level. We observed, that the importance of second polarization functions cannot be estimated from uncorrelated calculations.

Based on our calculations, we predict that all diatomic hydrides with six valence electrons right of and including BH and SiH$^+$ show temperature independent paramagnetism increasing with the positive charge and decreasing from the first row to the third row. Left of and including AlH and GeH$^+$ the molecules are diamagnetic. BeH$^-$ is on the borderline; in the largest basis set and the highest level of theory, we estimate it to be very weakly paramag-

TABLE XX. Contribution to the paramagnetic magnetizability ξ^P of GeH$^+$ from individual excitations at the RPA level. (See footnote a of Table XVIII.)

n	ΔE_n	$|\langle 0|l_\perp|n\rangle|$	GeH$^{+\,a}$ % of ξ^P
1	3.45	1.4110	85.62
2	11.32	0.0442	85.64
3	11.66	0.5804	89.93
4	14.74	0.1445	90.15
5	15.54	0.4897	92.44
6	17.04	0.3285	93.38
7	18.71	0.2576	93.90
8	21.51	0.1416	94.04
9	22.18	0.0795	94.08
10	22.73	0.3681	94.97

[a]For basis set 140.

TABLE XXI. Lowest $^1\Pi \leftarrow {}^1\Sigma^+$ excitation energy (in eV) as a function of the level of approximation and comparison with the experimental value.

	Basis set	RPA	SOPPA	CCDPPA	CCSDPPA	Experiment
BeH$^-$	94	0.65	0.56	0.83	0.84	
BH	105	2.65	2.44	2.79	2.81	2.87[a]
CH$^+$	103	2.64	2.47	2.93	2.95	3.07[b]
MgH$^-$	107	0.79	0.95	1.16	1.18	
AlH	106	2.99	2.80	3.03	3.05	2.95[a]
SiH$^+$	103	3.51	3.22	3.49	3.51	3.36[c]
GeH$^+$	104	3.46	3.16	3.36	3.39	

[a]Reference 24.
[b]Calculated from the spectroscopic constants in Ref. 31.
[c]Calculated from the spectroscopic constants in Ref. 32.

netic. The change in the magnetizability within the first or second row is dominated by the change in the diamagnetic contribution, which is related to the average size of the electronic cloud of the molecule. Going from the first to the third row the diamagnetic term increase again, because of the larger number of electrons. The paramagnetic contribution is reduced as a result of the increase in the excitation energy to the low lying $^1\Pi$ state. Overall the paramagnetism decreases from left to right and from top to bottom in the periodic system.

ACKNOWLEDGMENTS

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