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Scalar relativistic and spin-orbit effects in closed-shell superheavy-element monohydrides

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Relativistic and electron correlation effects are investigated for the closed-shell superheavy-element monohydrides RgH, $112H^+$, 113H, $114H^+$, 117H, $118H^+$, 119H, and $120H^+$. Periodic trends are discussed by comparing the calculated properties to the ones for the lighter elements. The size of the relativistic effects varies considerably between the different molecules with the *s*-block elements being dominated by scalar relativistic effects and the *p*-block elements dominated by spin-orbit effects. In most cases, relativistic effects are more important than electron correlation effects and both are nonadditive as one expects. $120H^+$ behaves in a counterintuitive way as it shows a relativistic bond-length expansion together with a large relativistic decrease in the dissociation energy. The reason behind this anomalous behavior is due to the relativistically diminished valence-7*d* participation in the 120-H bond.

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I. INTRODUCTION

The search for new chemical elements in the periodic table resulted in the recent discovery of the elements with nuclear charge 111 (Rg) and 112 by the GSI in Darmstadt [1–4] and most recently the elements with nuclear charge 113, 114, 115, 116, and 118 by the JINR group in Dubna [5–9]. Isotopes of these elements are extremely short lived, undergoing α decay within a second or less [10]. It is hoped that in near future more long-lived neutron-rich isotopes can be synthesized [11], making these elements better accessible to atom-at-a-time chemical experiments [12–14]. Here we note that the latest superheavy elements for which atom-at-a-time chemistry has been carried out are the ones with nuclear charge 112 [15–17] (α-decay half life $t_{1/2}^{\alpha}=3.8$ s for $^{283}112$ and 29 s for $^{285}112$) [18] and 114 ($t_{1/2}^{\alpha}=0.5$ s for $^{287}114$ and 2.7 s for $^{289}114$) [19].

Once these rare isotopes have been successfully prepared, one naturally is interested in their physical and chemical properties and how these elements compare to their lighter group members in the periodic table [12,13]. Recent advances in atomic spectroscopy made it possible to observe the atomic level structure of the element with nuclear charge $Z=100$ (^{255}Fm with a half life of 20.1 h) in an optical cell filled with argon buffer gas [20]. However, 2.7×10^{10} atoms of ^{255}Fm were used in these experiments and such a large number of isotopes is not available for experiments on the newly discovered superheavy elements. Here, one relies on chemistry on a one-atom-at-a-time scale [21]. Even if great progress has been made in trapping single atoms or molecules [22–26] and future experimental studies might well be able to explore spectroscopic properties of short-lived superheavy elements by such techniques, the current situation is that only few chemical studies are available for the transactinides [12,13]. Here we only mention recent atom-at-a-time experiments on Bh ($Z=107$) [27], Hs ($Z=108$) [28], element 112 [15–17], and very recently on element 114 [19].

In the meantime, we can study the chemistry and physics of superheavy elements by using theoretical methods [29–32]. However, the treatment of superheavy elements is less than trivial as a large number of electrons is involved and both relativistic and electron correlation effects need to be considered [32–39]. Considering the main-group superheavy elements, there are already a number of theoretical studies available on atoms and molecules, mostly using the relativistic pseudopotential approximation [40] or relativistic density-functional theory [41,42]. It is however important to provide benchmark calculations to test the various relativistic approximations in use [43,44]. We therefore decided to study the closed-shell superheavy-element monohydrides from Rg to element 120 at both the Dirac-Hartree-Fock and Dirac-Kohn-Sham level of theory and include electron correlation effects by a coupled-cluster procedure. Further, to discuss the importance of spin-orbit and scalar relativistic effects in electronic properties, we also carried out corresponding scalar relativistic (spin-free) as well as nonrelativistic calculations. We mention that some of the monohydrides have been studied before using various levels of relativistic approximations,

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TABLE I. Electron affinities (EA) and ionization energies (IP) of the superheavy elements (in eV) from four-component (R), scalar relativistic spin-free (SF) and nonrelativistic (NR) Hartree-Fock (HF) and Fock-space couple-cluster (FSCC) calculations.

Transition	Method	R	SF	NR
$\mathrm{Rg} \rightarrow \mathrm{Rg}^-$	HF	−0.210	−1.436	−0.071
	FSCC	−1.645	−2.533	−1.103
$112 \rightarrow 112^+$	HF	10.441	11.482	6.246
	FSCC	11.668	12.813	7.721
$113 \rightarrow 113^-$	HF	−0.090	0.633	0.514
	FSCC	−0.484	−0.087	−0.486
$114 \rightarrow 114^+$	HF	8.029	5.592	5.882
	FSCC	8.390	6.558	6.684
$117 \rightarrow 117^-$	HF	−0.602	−1.968	−2.475
	FSCC	−1.369	−2.765	−3.070
$118 \rightarrow 118^+$	HF	7.805	10.076	10.209
	FSCC	8.668	10.795	10.777
$119 \rightarrow 119^-$	HF	−0.092	0.064	0.053
	FSCC	−0.164	−0.162	0.157
$120 \rightarrow 120^+$	HF	5.011	4.903	3.647
	FSCC	5.470	5.407	3.998

i.e., RgH [41,42,45–49], $112\mathrm{H}^+$ [50–53], 113H [54–57], $114\mathrm{H}^+$ [52], 117H [56–58], and $118\mathrm{H}^+$ [52]. For example, spin-orbit effects in the series of neutral element hydrides from 113H to 118H were investigated by Lee and co-workers using a relativistic pseudopotential approximation [56]. Finally, we mention that there are only few atomic studies on electronic properties of the element with nuclear charges 119 [29,59–63] and 120 [29,63] and molecular calculations containing these two elements have, to our knowledge, not been carried out so far.

II. COMPUTATIONAL DETAILS

In order to investigate the molecular properties of the superheavy-element hydrides, we used nonrelativistic (NR), scalar relativistic spin-free (SF) [64–66], and relativistic Dirac-Coulomb (four-component) [67] theory (R) within wave-function-based methods applying the Hartree-Fock (HF) approximation, second-order many-body perturbation theory (MP2), and coupled-cluster theory including single and double substitutions (CCSD) and including the perturbative triples [CCSD(T)] to account for electron correlation [68], as well as density-functional theory using the local-density approximation (LDA) [69], the generalized gradient approximations (GGA) with the Perdew-Burke-Ernzerhof functional (PBE) [70], and the hybrid three-parameter Becke-Lee-Yang-Parr functional (B3LYP) [71–73]. In the Dirac picture, Kramers (time-reversal) symmetry was applied in the coupled-cluster procedure to save computer time [74]. The active orbital space included the occupied 6*s*, 6*p*, 7*s*, 6*d*, 7*p*, and 8*s* orbitals, with the virtual space being truncated above 100 a.u., i.e., we correlated 20 electrons for RgH and $112\mathrm{H}^+$, 22 electrons for 113H and $114\mathrm{H}^+$, 26 electrons for 117H and $118\mathrm{H}^+$, and 28 electrons for 119H and $120\mathrm{H}^+$. We neglected the $(SS|SS)$ two-electron integrals over the small components only and used Visscher's Coulomb correction instead [75]. A finite-size Gaussian nuclear model was chosen with the parameters listed by Visscher and Dyall [76].

All all-electron calculations were performed using extensive, uncontracted Gaussian-type dual basis sets tested to yield converged molecular properties with respect to the basis set extension toward softer functions. For the superheavy elements with nuclear charges 111–118, we started from Faegri's four-component basis sets [77] and arrived at $(28s/24p/20d/12f/3g)$ by adding a number soft *s*, *p*, and *d* functions as well as three *g* functions. Basis sets were not available for the elements 119 and 120. Therefore we adjusted new basis sets starting from the exponents for element 118 extended by three *s* functions and subsequently reoptimized the Gaussian exponents at the Dirac-Hartree-Fock (DHF) level using the program package GRASP [78] until the energy difference compared to the Dirac-Hartree-Fock basis set limit was smaller than 20 mH. For hydrogen, we used an uncontracted $(9s/5p/4d/1f)$ set of Gaussian functions obtained from Refs. [79,80]. The variational stability in all four-component calculations was ensured by using dual basis sets with the appropriate kinetic balance condition [81]. The basis sets are large enough to suppress the basis set superposition error, i.e., using the Boys-Bernardi counterpoise approximation [82], the bond distance at the scalar relativistic CCSD(T) level of theory increases only by 0.0009 Å for RgH and 0.000 12 Å for 117H.

The equilibrium bond lengths r_e and force constants k_e were obtained from polynomial fits of the potential curve around the minimum. The calculations of the dissociation energy D_e for the molecules were only carried out at the DHF, DHF-MP2, and DHF-CCSD(T) levels of theory and required more attention. First we carried out DHF, MP2, and CCSD(T) calculations for the intermediate dissociation of the hydrides into a proton (H^+) and the corresponding closed-shell superheavy element or ion, whose total electronic energy could be calculated with the program system DIRAC [67]. To obtain the correct dissociation energies, the ionization potential (IP) of hydrogen and the electron affinities (EA) or ionization potentials for the charged and neutral superheavy elements are required at different levels of theory, which we obtained from DHF and Fock-space coupled-cluster (FSCC) calculations [83,84] using the same basis sets. The considered dissociation paths for the investigated superheavy hydrides are as follows:

$$\mathrm{RgH} \rightarrow \mathrm{H}^+ + \mathrm{Rg}^-({}^1S_0) \rightarrow \mathrm{H} + \mathrm{Rg}({}^2D_{5/2}/{}^2S_{1/2}),$$

$$112\mathrm{H}^+ \rightarrow \mathrm{H}^+ + 112({}^1S_0) \rightarrow \mathrm{H} + 112^+({}^2D_{5/2}/{}^2S_{1/2}),$$

$$113\mathrm{H} \rightarrow \mathrm{H}^+ + 113^-({}^1S_0) \rightarrow \mathrm{H} + 113({}^2P_{1/2}),$$

$$114\mathrm{H}^+ \rightarrow \mathrm{H}^+ + 114({}^3P_0) \rightarrow \mathrm{H} + 114^+({}^2P_{1/2}),$$

$$117\mathrm{H} \rightarrow \mathrm{H}^+ + 117^-({}^1S_0) \rightarrow \mathrm{H} + 117({}^2P_{3/2}),$$

$$118\mathrm{H}^+ \rightarrow \mathrm{H}^+ + 118({}^1S_0) \rightarrow \mathrm{H} + 118^+({}^2P_{3/2}),$$

TABLE II. Bond distances r_e (in Å) and force constants k_e (in N m^{-1}) for the superheavy-element hydrides at various levels of theory.

	RgH		$112H^+$		113H		$114H^+$		117H		$118H^+$		119H		$120H^+$	
Method	r_e	k_e	r_e	k_e	r_e	k_e	r_e	k_e	r_e	k_e	r_e	k_e	r_e	k_e	r_e	k_e
Dirac-Coulomb																
DHF	1.520	454.0	1.526	390.9	1.698	136.6	1.716	194.6	1.970	150.5	1.904	191.9	2.529	53.1	2.291	118.8
MP2	1.505	427.4	1.525	397.7	1.701	134.1	1.728	165.8	1.902	166.6	1.868	201.2	2.402	61.6	2.226	112.5
CCSD	1.519	438.1	1.530	373.2	1.721	130.5	1.747	158.5	1.939	143.8	1.895	181.5	2.443	55.7	2.254	100.6
CCSD(T)	1.522	438.4	1.534	371.2	1.728	129.0	1.762	144.5	1.941	144.5	1.902	168.6	2.434	56.1	2.255	98.2
LDA	1.540	409.6	1.559	344.0	1.759	134.3	1.789	143.8	1.961	140.8	1.929	160.9	2.452	56.1	2.284	93.9
PBE	1.558	344.9	1.560	344.9	1.798	114.1	1.811	131.3	1.982	130.2	2.937	163.5	2.480	52.9	2.292	95.1
B3LYP	1.540	411.8	1.552	369.7	1.777	126.0	1.789	146.0	1.979	131.9	1.930	165.2	2.489	52.9	2.289	97.6
Scalar relativistic																
HF	1.513	488.9	1.531	403.2	2.013	93.4	1.911	171.3	1.793	267.8	1.774	277.1	2.601	46.7	2.328	99.6
MP2	1.501	504.4	1.527	414.1	1.939	110.5	1.881	178.8	1.767	268.7	1.757	275.6	2.450	56.0	2.254	102.8
CCSD	1.512	470.2	1.530	389.2	1.973	101.2	1.901	161.1	1.781	250.7	1.765	261.6	2.501	49.8	2.289	93.4
CCSD(T)	1.515	467.1	1.533	387.7	1.967	99.6	1.902	159.3	1.782	247.5	1.768	258.4	2.491	51.4	2.290	91.9
LDA	1.528	418.4	1.555	345.2	1.982	99.7	1.921	154.8	1.811	231.6	1.805	226.3	2.494	50.3	2.310	88.0
PBE	1.532	419.3	1.555	346.4	2.021	89.4	1.939	144.6	1.821	221.9	1.807	228.8	2.528	47.6	2.319	89.2
B3LYP	1.528	420.7	1.550	370.5	2.020	90.3	1.932	152.9	1.814	234.4	1.800	242.4	2.540	49.9	2.319	91.9
Nonrelativistic																
HF	2.019	109.0	1.952	157.2	2.079	121.4	1.980	182.2	1.847	269.3	1.823	284.9	2.761	35.8	2.231	90.3
MP2	1.876	133.9	1.888	166.6	2.032	123.0	1.955	193.1	1.817	294.3	1.797	296.6	2.633	39.7	2.156	97.1
CCSD	1.931	115.2	1.926	144.8	2.051	118.3	1.966	182.7	1.826	277.1	1.801	295.8	2.655	37.4	2.161	96.5
CCSD(T)	1.923	116.8	1.930	138.6	2.048	116.8	1.968	180.6	1.827	274.0	1.803	292.7	2.643	38.9	2.154	95.0
LDA	1.871	128.2	1.907	147.0	2.069	110.5	1.993	154.3	1.858	234.5	1.846	250.6	2.603	41.2	2.170	99.7
PBE	1.911	118.7	1.931	130.0	2.094	103.7	2.004	157.8	1.864	236.6	1.844	252.0	2.625	39.5	2.177	96.2
B3LYP	1.928	112.6	1.930	143.4	2.089	106.0	1.991	160.6	1.857	251.8	1.836	252.7	2.667	37.1	2.192	93.9

$$119\mathrm{H} \rightarrow \mathrm{H}^+ + 119^-({}^1S_0) \rightarrow \mathrm{H} + 119({}^2S_{1/2}),$$

$$120\mathrm{H}^+ \rightarrow \mathrm{H}^+ + 120({}^1S_0) \rightarrow \mathrm{H} + 120^+({}^2S_{1/2}).$$

The results of our atomic FSCC calculations are shown in Table I. We note that the nonrelativistic ground state for Rg and 112^+ is of ${}^2S_{1/2}$ symmetry with a $6d^{10}7s^1$ configuration, while the correct relativistic ground state is of ${}^2D_{5/2}$ symmetry ($6d^97s^2$) [29,85]. Further, positive electron affinities indicate that the electron in the negatively charged species is not bound and in the complete basis set limit, it should be zero. Nevertheless, we use these small positive electron affinities for correcting our dissociation energies. Small errors which come from the different coupled-cluster treatment for the molecules and dissociated atoms are within the basis set and correlation error. For example, for RgH and 113H, we calculate dissociation energies of 2.052 and 3.435 eV at the nonrelativistic level of theory, respectively, whereas from unrestricted coupled CCSD(T) calculations [86], we obtain 2.139 and 3.511 eV, respectively.

We also considered the Gaunt term of the Breit interaction [87,88] as a small correction to the usual Coulomb interaction between two electrons. However, the changes in bond lengths and other properties are much smaller compared to the errors introduced by the use of finite basis sets, restricted orbital space in the correlation procedure or corrections from noniterative triples or higher substitutions in the coupled-cluster procedure, and were therefore neglected. For example, for RgH and 117H, the bond lengths increased by 6.2×10^{-4} Å and 9.3×10^{-4} Å, respectively, at the DHF level of theory upon inclusion of the Gaunt term.

III. RESULTS AND DISCUSSION

The results of our molecular calculations are summarized in Tables II–IV. Before we discuss the properties of the superheavy-element hydrides with respect to their lighter congeners in detail, let us compare our relativistic four-component calculations to previously published results using various models of approximations.

There are a number of papers concerning RgH [41,42,45–49]. Here we only mention Dolg *et al.* who obtained from benchmark spin-orbit coupled pseudopotential calculations including electron correlation at the CCSD(T) level of theory $r_e=1.529$ Å, $k_e=409.8$ N m^{-1}, and $D_e=2.83$ eV [47]. This is in excellent agreement with our all-electron DHF-CCSD(T) treatment. Earlier all-electron DHF-CCSD(T) results by Seth and Schwerdtfeger ($r_e=1.523$ Å, $k_e=419.7$ N m^{-1}, and $D_e=2.83$ eV [45]) are in similar good agreement. Concerning $112H^+$ Mosyagin *et al.* obtained

TABLE III. Dissociation energies D_e (in eV) for the superheavy-element hydrides at the DHF and CCSD(T) level of theory using the atomic values listed in Table I.

Method	RgH	$112H^+$	113H	$114H^+$	117H	$118H^+$	119H	$120H^+$
Dirac-Coulomb								
DHF	1.675	2.583	0.546	0.192	0.892	0.698	0.583	0.580
CCSD(T)	2.989	3.776	1.774	1.402	2.170	2.181	1.793	1.804
Scalar relativistic								
HF	2.658	3.462	2.077	2.261	1.833	2.144	0.474	0.464
CCSD(T)	3.721	4.812	3.264	3.635	3.246	3.551	1.656	1.676
Nonrelativistic								
HF	0.906	0.688	2.032	2.648	2.180	2.505	1.101	2.408
CCSD(T)	2.052	1.786	3.435	3.755	3.616	3.914	2.242	3.514

$r_e=1.537$ Å, $k_e=387.4$ N m^{-1}, and $D_e=3.96$ eV using Fock-space coupled-cluster calculations within a generalized relativistic effective core potential scheme [53], again in very good agreement with our results. For comparison, Seth *et al.* obtained $r_e=1.517$ Å, $k_e=419.4$ N m^{-1}, and $D_e=4.09$ eV [50] and Nash obtained $r_e=1.583$ Å and $D_e=3.50$ eV [52], both using CCSD(T) calculations but differently adjusted relativistic pseudopotentials (RPPs). 113H has been investigated before by Seth *et al.* ($r_e=1.789$ Å, $k_e=109$ N m^{-1} and $D_e=1.44$ eV) using four-component CCSD(T) [54] but applying much smaller basis sets. Lee *et al.* ($r_e=1.759$ Å and $D_e=1.46$ eV) performed two-component CCSD(T) using RPPs [56] and Choi and co-workers ($r_e=1.755$ Å, $k_e=132.5$ N m^{-1}, and $D_e=1.53$ eV) used spin-orbit DFT (SO-DFT) in connection with RPPs [55,57]. For $114H^+$ we only have one paper published by Nash ($r_e=1.73$ Å and $D_e=1.01$ eV) using a RPP in a CCSD(T) scheme [52]. For 117H, we mention three different calculations by Lee *et al.* ($r_e=1.949$ Å and $D_e=1.79$ eV) obtained by using a two-component RPP within a CCSD(T) procedure [56], by Choi *et al.* ($r_e=1.957$ Å, $k_e=143.2$ N m^{-1}, and $D_e=1.58$ eV) using SO-DFT [57], and by Peng *et al.* ($r_e=1.988$ Å, $k_e=128.3$ N m^{-1}, and $D_e=2.04$ eV) using a Dirac (four-component) Kohn-Sham scheme [58]. Last we cite results for $118H^+$ by Nash ($r_e=1.992$ Å and $D_e=1.60$ eV) obtained by CCSD(T) calculations using a RPP [52], which deviate substantially from our values indicating problems in the pseudopotential approximation used. Table II also shows that density-functional theory performs reasonably well for these superheavy elements, with perhaps the B3LYP functional performing best.

The calculated relativistic and electron correlation effects for various properties are shown in Table V. We observe clear trends within the series of superheavy-element hydrides. For the bond distances, relativistic effects are much larger than electron correlation effects with the largest bond contractions calculated for RgH and $112H^+$ due to scalar relativistic contributions. For these two compounds, spin-orbit contributions to the bond distance are very small. Moreover, scalar relativistic effects to the bond distance are much larger for RgH and $112H^+$ compared to the other two *s*-block element hydrides 119H and $120H^+$, which stems from the relativistic maximum at the group 11 or 12 elements along a period in the periodic table (see Refs. [32,89–92] for a detailed discussion). The situation changes completely for the *p*-block element hydrides. Here spin-orbit coupling becomes the dominant relativistic contribution for bond distances, with scalar relativistic effects being much smaller but still larger compared to electron correlation. This is expected from the very large spin-orbit splitting in the $7p$ shell [32], i.e., FSCC calculations by Kaldor and co-workers give a $^2P_{1/2}/^2P_{3/2}$ splitting for element 113 of 2.79 eV [93] and Dirac-Fock-Breit calculations give a $^2P_{3/2}/^2P_{1/2}$ splitting of 9.91 eV for element 117. Hence we see a spin-orbit bond contraction for 113H and $114H^+$ due to the spin-orbit contraction of the $7p_{1/2}$ shell and a spin-orbit bond lengthening for 117H and $118H^+$ due to the spin-orbit expansion of the $7p_{3/2}$ shell. These spin-orbit effects are greatly diminished when moving from the neutral to the isoelectronic positively charged molecule, i.e., from 113H to $114H^+$ and from 117H to $118H^+$, as depletion of electron density of either the $7p_{1/2}$ or $7p_{3/2}$ shell reduces these relativistic effects.

An exception to the whole trend is found for $120H^+$ where we see a *relativistic bond expansion* and not a contraction as one might expect. As a consequence, we do not see a change in the trend of bond lengths due to relativistic effects for the positively charged group 2 hydrides in contrast to the group 1 series of hydrides (cf. Fig. 1). In order to verify this rather intriguing result, we investigated FrH, RaH^+, and BaH^+ as

TABLE IV. Dipole moments μ_e (in Debye) for the neutral superheavy-element hydrides at the DHF and CCSD(T) level of theory.

Method	RgH	113H	117H	119H
Dirac-Coulomb				
DHF	−0.309	0.507	−2.544	−6.847
CCSD(T)	−0.013	0.067	−1.943	−5.605
Scalar relativistic				
HF	−0.544	−2.797	−0.700	−7.698
CCSD(T)	−0.139	−2.467	−0.617	−5.488
Nonrelativistic				
HF	−5.792	−0.499	0.261	−9.902
CCSD(T)	−4.213	−0.819	0.070	−9.233

TABLE V. Relativistic effects at the CCSD(T) level of theory and electron correlation effects at the DHF level of theory for bond distances r_e (in Å), force constants k_e (in N m^{-1}), and dissociation energies D_e (in eV) for the superheavy-element hydrides. SR: scalar relativistic effects, SO: spin-obit effects, Corr: Correlation effects.

	RgH	$112H^+$	113H	$114H^+$	117H	$118H^+$	119H	$120H^+$
$\Delta r_e^{\mathrm{Corr}}$	0.001	0.008	0.030	0.047	−0.029	−0.002	−0.095	−0.036
Δr_e^{SR}	−0.408	−0.397	−0.081	−0.066	−0.044	−0.035	−0.152	0.135
Δr_e^{SO}	0.007	0.000	−0.240	−0.140	0.158	0.134	−0.057	−0.034
$\Delta r_e^{\mathrm{SR+SO}}$	−0.401	−0.396	−0.321	−0.206	0.114	0.099	−0.209	0.101
$\Delta k_e^{\mathrm{Corr}}$	−15.6	−19.7	−7.6	−50.1	−6.1	−23.3	3.1	−20.6
Δk_e^{SR}	350.4	249.1	−17.1	−21.3	−26.5	−34.3	12.5	−3.6
Δk_e^{SO}	−28.8	−16.5	29.4	−14.8	−103.1	−89.8	4.8	6.4
$\Delta k_e^{\mathrm{SR+SO}}$	321.6	232.6	12.2	−36.2	−129.6	−124.1	17.2	3.3
$\Delta D_e^{\mathrm{Corr}}$	1.314	1.193	1.228	1.210	1.278	1.483	1.209	1.224
ΔD_e^{SR}	1.669	3.027	−0.172	−0.120	−0.370	−0.363	−0.589	−1.838
ΔD_e^{SO}	−0.733	−1.063	−1.489	−2.233	−1.076	−1.370	0.137	0.128
$\Delta D_e^{\mathrm{SR+SO}}$	0.937	1.990	−1.661	−2.353	−1.446	−1.733	−0.449	−1.710
$\Delta \mu_e^{\mathrm{Corr}}$	0.322		−0.440		−0.601		−1.242	
$\Delta \mu_e^{\mathrm{SR}}$	4.074		−1.648		−0.687		3.745	
$\Delta \mu_e^{\mathrm{SO}}$	0.126		2.534		−1.326		−0.117	
$\Delta \mu_e^{\mathrm{SR+SO}}$	4.200		0.886		−2.013		3.628	

well, but only at the B3LYP level of theory using a Dyall triple-zeta basis set with three *g* functions. For FrH, we get similar results compared to 119H showing a relativistic bond contraction, i.e., r_e=2.537 Å (Dirac), 2.547 Å (SF), and 2.563 Å (NR). However, for RaH$^+$, we obtain r_e=2.234 Å (Dirac), 2.241 Å (SF), and 2.167 Å (NR). In comparison, for BaH$^+$ we obtain r_e=2.137 Å (Dirac), 2.135 Å (SF), and 2.111 Å (NR). Hence RaH$^+$ shows exactly the same trend in relativistic effects compared to 120H$^+$. What is the origin of this relativistic bond expansion in view of the relativistic valence *s* contraction?

The answer lies perhaps in a previous study on BaH$^+$ and RaH$^+$ by Pyykkö and co-workers [96,97], who emphasized the importance of the vacant *d* orbitals in the bonding, which we like to analyze in more detail here for 120H$^+$. Table VI shows the gross atomic charges obtained from a Mulliken population analysis. What is interesting here is not only the large charge flow from the neutral hydrogen atom to the metal atom due to relativistic effects for the compounds RgH (Rg becomes negatively charged), 113H, and to a lesser extent 119H, but also the rather large positive charge at element 120 indicating that 120H$^+$ is best described as 120^{2+}H$^-$. If we look at the first and second ionization potentials for element 120, which are 5.47 eV (see Table I) and 11.58 eV (from the first ionization potential in Table I and the double-ionization potential calculated recently by Dinh *et al.* [63]), respectively, we see that the second ionization potential is relatively small, in fact, smaller than the ionization potential of the hydrogen atom (13.595 eV [98]). Depleting almost completely the valence *s* shell will significantly reduce relativistic effects [99] as this is the case for 120H$^+$. However, similar small ionization potentials are found for all the group 2 elements and we should therefore expect similar small relativistic effects for the lighter elements. This is indeed the case for RaH$^+$ and BaH$^+$ as discussed above and has been demonstrated earlier for these two molecules in calculations by Pyykkö and co-workers [96,97]. We note that the scalar relativistic valence populations for the vacant *d* orbital at the heavy atom at the HF level of theory for 120H$^+$, RaH$^+$, and BaH$^+$ are −0.02, −0.10, and −0.15, respectively. In contrast, at the nonrelativistic level we have −0.14, −0.19, and −0.19,

TABLE VI. Mulliken charges at the superheavy element at the HF and B3LYP level of theory at he relativistic Dirac (R), scalar relativistic spin-free (SF), and nonrelativistic (NR) level of theory.

Transition	Method	R	SF	NR
RgH	HF	−0.25	−0.25	0.66
	B3LYP	−0.43	−0.44	0.48
$112H^+$	HF	0.49	0.51	1.47
	B3LYP	0.37	0.37	1.29
113H	HF	0.16	0.60	0.62
	B3LYP	0.16	0.55	0.52
$114H^+$	HF	0.89	1.53	1.52
	B3LYP	0.90	1.47	1.45
117H	HF	0.52	0.43	0.39
	B3LYP	0.42	0.39	0.34
$118H^+$	HF	1.36	1.29	1.25
	B3LYP	1.28	1.26	1.20
119H	HF	0.77	0.77	0.89
	B3LYP	0.61	0.59	0.83
$120H^+$	HF	1.75	1.76	1.92
	B3LYP	1.60	1.58	1.94

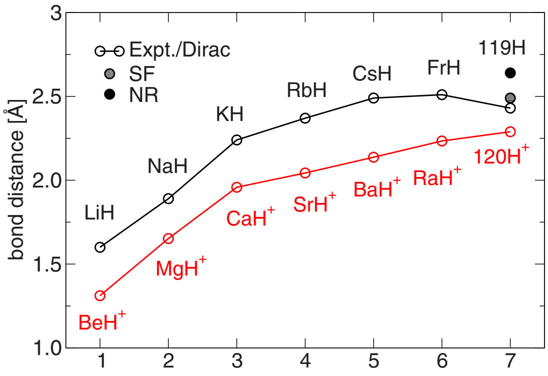

FIG. 1. (Color online) Bond distances for the groups 1 (MH) and 2 (MH^+) metal hydrides. Experimental values from Ref. [94]. All other values from our calculations or from Ref. [95].

respectively. Hence, going down the group 2 elements, the relativistic valence-*s* contraction and the relativistic expansion of the vacant *d* orbitals open up the *s*-*d* gap and diminish the valence *d* participation in the bond, thus rationalizing the relativistic increase in the bond length observed for $120H^+$. However, removing the most diffuse *d* functions reduces substantially the bond distance at both the nonrelativistic and relativistic levels of theory and diminishes the relativistic bond expansion in $120H^+$ which again is counterintuitive. Hence there seems to be a subtle interplay between different orbital contributions and corresponding relativistic effects. We further note that for $120H^+$, the vacant *f* and *g* orbitals show negligible populations.

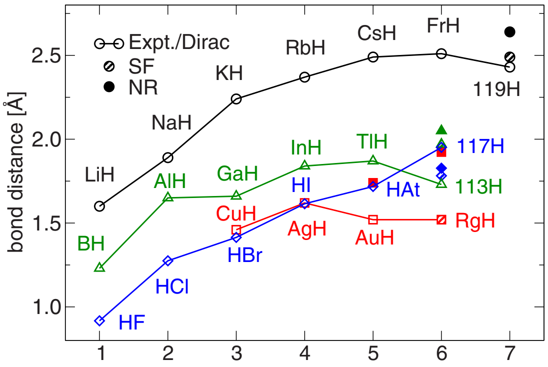

FIG. 3. (Color online) Comparison of the calculated relativistic (circle), spinfree (diamond), and nonrelativistic (square) CCSD(T) bond distances for RgH, 117H, 113H, and 119H with experimental values for the lighter homologes. Experimental values (circle) are taken form [94], the nonrelativistic value of AuH form [44], and the relativistic value for AtH from [100], respectively.

The bond distances along the seventh period main-group hydrides RgH, $112H^+$, 113H, $114H^+$, 117H, and $118H^+$, as well as 119H and $120H^+$, are compared in Fig. 2 at different levels of theory, which nicely shows the interplay between scalar relativistic and spin-orbit effects as discussed above. Note the close proximity of the HF and coupled-cluster curves which shows that relativistic effects are more important than electron correlation. Figure 3 shows the trend in bond distances down the periodic table for the neutral element hydrides. We clearly see changes in trends between the elements Fr and 119, as well as Ag and Au, due to a scalar relativistic valence *s* contraction causing bond contractions, between the elements Tl and 113 due to a spin-orbit $7p_{1/2}$ contraction causing a large bond contraction for 113H, and a large increase in bond length for 117H due to a spin-orbit $7p_{3/2}$ expansion (see also Ref. [37] for a detailed discussion on relativistic effects in bond distances). The trend in bond distances down a specific group of elements in the periodic table shown in Fig. 3 closely resembles the trends in atomic radii published by Fricke [29] and the more recently published trends in covalent radii published by Pyykkö and Atsumi [48].

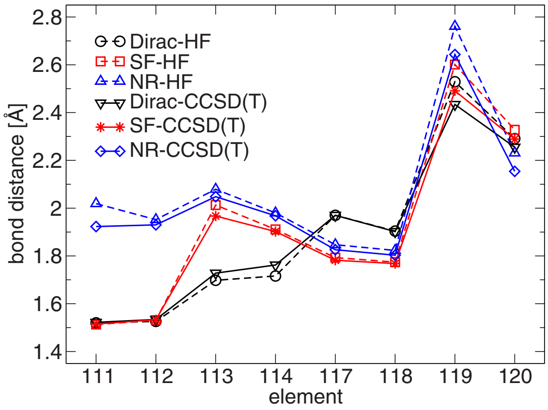

FIG. 2. (Color online) Comparison of calculated relativistic (Dirac), SF scalar relativistic, and NR HF and CCSD(T) bond distances across the seventh period main-group hydrides RgH, $112H^+$, 113H, $114H^+$, 117H, and $118H^+$, as well as 119H and $120H^+$.

The force constants show similar relativistic effects as shown in Table V. The corresponding trends across and down the periodic table are shown in Figs. 4 and 5. Here we see rather large relativistic effects for the groups 11 and 12 element hydrides leading to a strong increase in force constants causing large changes in periodic trends already at gold, which has been discussed in detail before [99,101]. For 117H and $118H^+$, we calculate a very large relativistic decrease in the force constants, leading to a monotonic de-

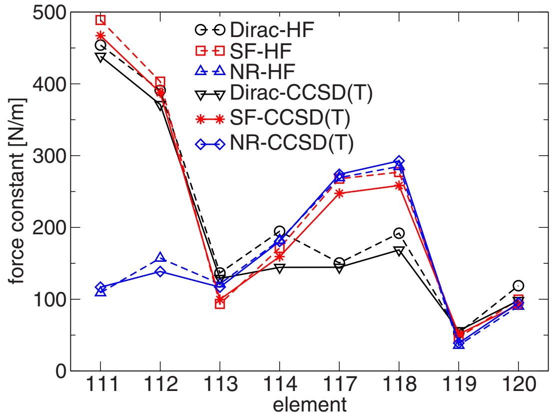

FIG. 4. (Color online) Comparison of calculated relativistic (Dirac), spinfree scalar relativistic (SF), and nonrelativistic (NR) HF and CCSD(T) force constants across the seventh period main-group hydrides RgH, $112H^+$, 113H, $114H^+$, 117H, and $118H^+$, as well as 119H and $120H^+$.

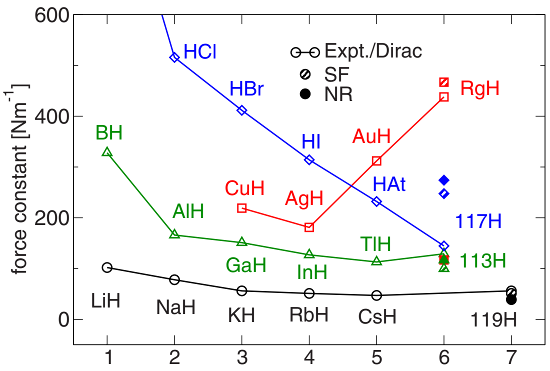

FIG. 5. (Color online) Comparison of the calculated relativistic (circle), spinfree (diamond), and nonrelativistic (square) CCSD(T) force constants for RgH, 113H, 117H, and 119H with experimental values for the lighter homologes. Experimental values (circle) are taken form Ref. [94] and the relativistic value for AtH from Ref. [100], respectively.

crease in the force constants down the group 17 series of elements as shown in Fig. 5. The rather small force constant calculated for 117H is in agreement with the rather small dissociation energy calculated at the four-component CCSD(T) level of theory (Fig. 6).

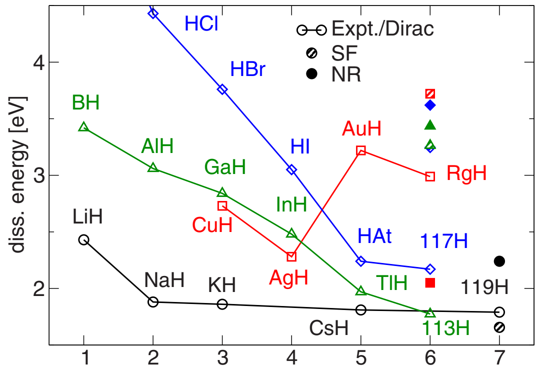

FIG. 6. (Color online) Comparison of the calculated relativistic (circle), spinfree (diamond), and nonrelativistic (square) CCSD(T) dissociation energies for RgH, 113H, 117H, and 119H with experimental values for the lighter homologes. Experimental values (circle) are taken form [94] and the relativistic value for AtH from [100], respectively.

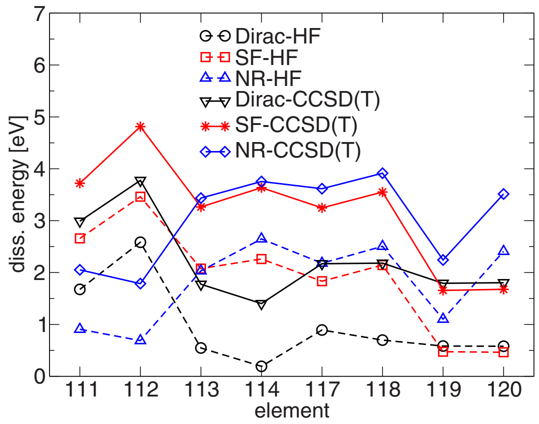

FIG. 7. (Color online) Comparison of calculated relativistic (Dirac), spinfree scalar relativistic (SF), and nonrelativistic (NR) HF and CCSD(T) dissociation energies across the seventh period main-group hydrides RgH, $112H^+$, 113H, $114H^+$, 117H, and $118H^+$, as well as 119H and $120H^+$.

The dissociation energies are more difficult to discuss, as relativistic effects for the separated atoms have to be considered and electron correlation effects are significant as one expects. For both RgH and $112H^+$, the large scalar relativistic effect is partly cancelled by spin-orbit coupling due to a change in the electronic configuration from $^2S_{1/2}(6d^{10}7s^1)$ to $^2D_{5/2}(6d^97s^2)$ for the elements Rg and 112^+ [29,85]. Nevertheless, there is a large relativistic increase in the dissociation energy for RgH and $112H^+$ as shown in Fig. 7, leading, for example, to a dissociation energy of RgH larger than that of AgH (but smaller than that of AuH due to the spin-orbit effects as just discussed). The *p*-block element hydrides all undergo relativistic destabilization effects mainly due to spin-orbit stabilization at the atomic level. We also point out that the very large scalar relativistic destabilization of $120H^+$ (and to a lesser extend for 119H) again is rather unexpected and contrary to the dissociation energies calculated for the group 11 or 12 element hydrides. Finally, we note that the large changes in the Mulliken charges and corresponding charge flow from the hydrogen to the superheavy element (except for $118H^+$) result in rather large changes (especially for RgH) in the dipole moments as can be seen in Table IV.

IV. CONCLUSION

We discussed scalar relativistic and spin-orbit effects for closed-shell superheavy-element hydrides in detail and described the trends in properties across and down the periodic table. While the trends in the groups 11 and 12 elements hydrides are dominated by scalar relativistic effects, the *p*-block elements are clearly dominated by spin-orbit effects. For 119H and $120H^+$, relativistic effects in the valence 7*s* shell are much smaller, and for $120H^+$, we observe a relativistic bond expansion. The relativistic four-component coupled-cluster calculations presented in this work will serve as future benchmark values for theoretical investigations into superheavy element containing compounds.

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