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A Relativistic Muffin-tin Free Xα Molecular Orbital Study of Metal Tetrakis Tetrahydroborates: $M(BH_4)_4$, M = Zr, U

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Abstract

Muffin-tin free DV-Xα molecular orbital calculations employing self-consistent numerical basis sets have been performed for the tetrakis tetrahydroborates of zirconium and uranium. For the latter compound, both a nonrelativistic and a fully relativistic solution have been obtained. These calculations essentially confirm the results of a recent extensive Xα-SW study on the electronic structure of tetrahydroborates. Very good agreement with experimental ionization potentials is found in the present calculation. The assignment of the most important ligand metal bonding orbitals to the first PE band of $Zr(BH_4)_4$ supports that of the Xα-SW study, but is at variance with the results of a previous STO-DV-Xα investigation. A relativistic treatment is mandatory for a proper description of the metal ligand bonding in the uranium complex. In the nonrelativistic calculation the contribution of U 5f orbitals to metal ligand covalency is overestimated, the participation of the U 6d orbitals in such bonding is underestimated. These findings parallel the results of a previous Xα-SW study on uranocene, $U(C_8H_8)_2$, where this effect has been rationalized as a pecularity of the Xα method.

1. Introduction

In a recent quasirelativistic Xα scattered-wave (SW) study [1] we have analyzed the electronic structure of a series of metal tetrakis tetrahydroborates, $M(BH_4)_4$, M = Zr, Hf, Th, U. Due to the characteristics of the BH_4 ligands, unusually strong ligand–metal π bonding has been found [1] resulting in an ordering of the ligand-derived molecular orbitals which differs from that of tetrahedral d metal complexes with dominating σ bonding. For the actinide borohydrides included in the study [1] metal f orbitals were shown to participate in the bonding of the ligands, again with characteristic effects on the ligand-derived molecular orbitals.

The only other electronic structure calculation on these compounds previously available for comparison was a DVM study of $Zr(BH_4)_4$ utilizing a Slater-type orbital (STO) basis [2]. The results from both computational methods showed one striking difference concerning the energetic ordering of those two MOs which afford the strongest metal ligand interaction, $2t_2$ and 1e. Besides entailing a differing assignment of the photoelectron (PE) spectrum the muffin-tin free DVM results could be taken to question the conclusions on the bonding in metal borohydrides obtained in the SW study [1].

The metal borohydrides exhibit a rather open structure due to tetrahedral coordination both around the central metal atom and within the ligands. Consequently, the muffin-tin approximation underlying the SW formalism leads to inaccuracies in the description of the electronic potential. Although these deficiences may be checked and reduced through a judicious choice of overlapping spheres [1, 3], errors cannot be completely excluded by such SW model studies alone.

Furthermore, given the unusual level ordering of the STO-DV calculation which places the purely π bonding 1e orbital 1.5 eV below the $2t_2$ level, an independent muffin-tin free electronic structure study of the metal borohydrides seemed desirable and will be presented here.

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We chose the DV-Xα method employing a numerical basis [4], an approach that has proven to yield accurate results for heavy-metal complexes in general [5] and has already been applied to MX_4-type compounds, too [6]. A further advantage of this methodology is the fact that a solution of the Dirac equation is available, providing an improvement over the previous quasirelativistic treatment [1] which was unable to account for spin-orbit effects in a self-consistent way [7]. The molecules we selected for an investigation are $Zr(BH_4)_4$ as transition metal and $U(BH_4)_4$ as actinide borohydride.

2. Computational Details

The discrete variational (DV) Xα method applied in this work is of the classical LCAO type. Symmetrized linear combinations of numerical free atom/ion wavefunctions are used as basis set [8]. The so-called self-consistent charge (SCC) [9] procedure has been used to converge the SCF equations, whereby a shape approximation of overlapping spherical functions was employed to represent the true molecular density. To reduce the computational effort the core charge densities B([He]), Zr([Ar] $3d^{10}$) and U([Xe]-$4f^{14}$ $5d^{10}$ $6s^2$) were kept frozen. The same idealized molecular geometries as in the previous SW study have been used. They had been obtained from electron and neutron diffraction analyses of $Zr(BH_4)_4$ [10] and $U(BH_4)_4$ [11].

The DV method offers the opportunity to systematically improve the basis set used in the representation of the wavefunctions and the potentials [8]. In this way, the solution of the SCF equations becomes more and more exact. In the present work this has been done for all calculations separately to the extent where a Mulliken population analysis of the resulting orbitals agreed to about two decimals with the electronic configuration underlying the generation of the atomic orbital basis functions. As an exception to this procedure hydrogen basis functions corresponding H $1s^1$ were used throughout this study. To localize the more diffuse valence states a potential well of depth 40.8 eV with an inner radius of 4.0 a.u. and an outer radius of 6.0 a.u. was added to the atomic potential. The resulting self-consistent atomic configurations for nonrelativistic $Zr(BH_4)_4$ and $U(BH_4)_4$ as well as relativistic $U(BH_4)_2$ are then practically identical to the results of the population analysis displayed in Table IV (for a discussion see Section 3.3).

The exchange parameter α was set to a uniform value of 0.7 in all calculations. The functions were sampled at 5159 points in the calculation of $Zr(BH_4)_4$, at 5570 and 5810 points in the nonrelativistic and relativistic calculations of $U(BH_4)_4$, respectively. Slater's transition state procedure [12] was used to compute ionization energies.

Incorporation of the spin-orbit interaction in the Dirac treatment of $U(BH_4)_4$ leads to the molecular symmetry group T_d^* with double-valued representations Γ_6, Γ_7, and Γ_8 [13]. Their correspondence with single-valued representations of the non- and quasirelativistic treatment is as follows:

$a_1 \rightarrow \Gamma_6$
$e \rightarrow \Gamma_8$
$t_1 \rightarrow \Gamma_6 + \Gamma_8$
$t_2 \rightarrow \Gamma_6 + \Gamma_7$

Besides the spin-orbit splitting of nonrelativistic levels, further mixing may occur in the relativistic case due to more symmetry allowed interactions among the various atomic orbitals. The relativistic level spectrum will therefore show spin-orbit, covalency and crystal field effects all superimposed. A major part of Section 3.2 will be dedicated to sorting out the relative magnitude of and the interplay between these effects.

3. Results and Discussion

In the first part of this section we will explain the new DVM results for $Zr(BH_4)_4$ in the light of recent SW [1] and older DVM [2] calculations. The remainder of the section will then be devoted to the presentation of the fully relativistic DVM calculation of $U(BH_4)_4$ and its comparison to the corresponding nonrelativistic results. Differences to the transition metal compound $Zr(BH_4)_4$ will be pointed out and reference will be made to the SW treatment of these compounds [1].

3.1. $Zr(BH_4)_4$ – The Ordering of the π Bonding Levels

The SW treatment of $Zr(BH_4)_4$ [1] has been shown to yield qualitatively rather similar results than an earlier, muffin-tin free DV-Xα calculation [2]. However, aside from orbital energy shifts of up to 4 eV the two calculations were incompatible in one important aspect. The ligand p-like levels [1] 1e and $2t_2$ were predicted by the DV results to be in the reverse order of the SW calculation, namely $1e < 2t_2$ [2], leading to a contradictory assignment of the PE spectrum, as already mentioned above. (For the numbering of the valence MOs, see Table I and ref. 1.)

First of all we observe that in the STO-DV calculation [2] the ligand p-like manifold $2t_2$, 1e, $2a_1$, $3t_2$, $1t_1$ was predicted to be 3.5 eV wide as compared to a width of 1.8 eV derived from the SW calculation. The experimentally derived value of 2.2 eV is closer to the SW value. This suggests that for some unknown reason the previously given STO-DV description [2] of the 1e level is erroneous, at least relative to the other p-like orbitals. The latter may be concluded from the fact that raising the 1e orbital by about 1.5 eV would yield the presumable ordering $2t_2 < 1e$ and, at the same time, a reasonable width of the p-like manifold.

It has been shown [3] that the order $2t_2 < 1e$ is stable in the SW description against even drastic changes of the employed muffin-tin radii. The SW ordering, if fallacious, would entail a differential muffin-tin error of up to 2 eV on one level. Such an error would shed serious doubts on the SW results in total and on the interpretation of the bonding deduced from them [1].

TABLE I. DV-Xα Ground State Molecular Orbital Energies (in eV) and Orbital Population Analysis[a] for $Zr(BH_4)_4$

Orbital	Energy	Zr[b]			B		H_B	H_T
		4p	4d	5s	2s	2p		
$4t_2$	−3.80		0.64			0.20	0.10	0.06
2e	−3.90		0.82			0.12	0.06	
$1t_1$[c]	−9.90					0.45	0.55	
$3t_2$	−9.92		0.04		0.04	0.51	0.02	0.39
$2a_1$	−10.20			0.02	0.08	0.48		0.42
1e	−11.32		0.17			0.37	0.46	
$2t_2$	−11.70		0.12			0.29	0.58	
$1t_2$	−16.33	0.02	0.05		0.40	0.05	0.42	0.06
$1a_1$	−17.23				0.38	0.09	0.47	0.04

[a] Only populations larger than 0.01 are listed. [b] The population of the core-like Zr 4s AO in all valence orbitals is negligible. [c] Highest occupied molecular orbital.

In Table I we display the orbital energies and population analysis from the present DV investigation on $Zr(BH_4)_4$. This DV calculation with its practically self-consistent basis set features the same ordering $2t_2 < 1e$ as found in the SW calculation [1]. We may therefore conclude that this level ordering is definitely not an effect of the muffin-tin approximation to the electronic potential.

In an attempt to test the basis set dependence of the level ordering, we repeated the calculation for three additional basis sets, characterized by atomic configurations ranging from very ionic to purely neutral configurations ranging from very ionic to purely neutral constituents, namely:

(i) Zr $4d^0$ $5s^0$, B $2s^1$ $2p^3$, H $1s^1$
(ii) Zr $4d^0$ $5s^0$, B $2s^0$ $2p^0$, H $1s^2$
(iii) Zr $4d^2$ $5s^2$, B $2s^2$ $2p^1$, H $1s^1$

All these basis sets lead to the same ordering $2t_2 < 1e$ with a level splitting of at least 0.4 eV, the main effect being a largely uniform shift of the orbital energy spectrum. Even using such very different basis sets, we were unable to reproduce the level ordering of the earlier STO-DV calculation [2] which must therefore remain without explanation at the moment.

Close inspection of Table I reveals a large extent of agreement between the SW [1] and the present DV results. Absolute ground state orbital energies differ by about 1 eV in the ligand s-like levels $1a_1$ and $1t_2$, and by about 1.7 eV in the ligand p-like orbitals $2t_2$, 1e, $2a_1$, $2t_2$, and $1t_1$. The relative spacings, however, turn out to be quite similar: width of s-like manifold: 0.9 eV (DV) *versus* 0.7 eV (SW); width of p-like manifold: 1.8 eV (DV and SW); separation between both manifolds: 4.6 eV (DV) *versus* 3.8 eV (SW). Most importantly, the level ordering of both methodologies is identical.

At this point it may be appropriate to recall the level ordering in the p-like manifold of tetrahedral transition metal complexes as expected from simple molecular orbital arguments [14–16]. The p_σ orbitals generate an a_1 and a t_2 level, the p_π orbitals levels of type t_2, e and t_1. The symmetry-adapted ligand orbitals will interact with metal orbitals of the same symmetry type. Assuming that the metal d orbitals (symmetry types e and t_2) provide the dominant interaction partners, one expects the 1e orbital to be stabilized by π bonding only, whereas the $2t_2$ level is able to profit both from σ- and π-type interaction. The $2a_1$ orbital may contribute somewhat to metal–ligand σ bonding through interaction with the metals valence orbital. The remaining ligand derived $1t_1$ and $3t_2$ are essentially non-bonding, the former in a strict sense since it finds no interaction partner in a transition metal complex (for an f-element complex, see ref. 1 and below).

In a strongly σ bonding complex one would therefore deduce the ordering in the p-like manifold to be $2t_2 < 2a_1$, $1e < 3t_2 < 1t_1$. However, for dominating π interaction one might expect the ordering $1e < 2t_2 < 2a_1 < 3t_2 < 1t_1$, since the metal–ligand π overlap is larger for an e ligand orbital than for the corresponding t_2 orbital by a factor of $\sqrt{3}$ [14].

Thus far, our considerations have focused exclusively on metal–ligand interaction, neglecting any ligand–ligand interaction. They are therefore certainly oversimplified, especially since the metal–ligand bonding is relatively weak. As a criterion for this bonding we may take the metal population in the levels $2t_2$ (0.12) and 1e (0.17). These populations are quite small when compared to a complex with strong metal–ligand interaction such as MnO_4^-, where the corresponding populations are found to be 0.44 and 0.50, respectively [17]. The importance of ligand–ligand interaction has already been stressed in the analysis of photoelectron spectra of related tetrahalide complexes, e.g. in $ZrCl_4$ [15]. The effect of this interaction can be read off from the level spectrum of the 'empty' cluster $(BH_4)_4$ which is available from a SW calculation [1, 3]. The p-like manifold of this cluster shows an overall splitting of about 1 eV, the level ordering being $2t_2(\pi) \lesssim 2a_1 < 1e < 3t_2(\sigma) < 1t_1$. (For the two t_2 levels their dominant characteristic has been given). Note that ligand–ligand π interaction strongly favours the $2t_2(\pi)$ over the $1e(\pi)$ level [14].

In the present calculation we find the preferentially π bonding $2t_2$ orbital and the purely π bonding 1e level lying energetically well below the $2a_1$ level, the preferentially σ bonding $3t_2$ and the non-bonding $1t_1$ orbitals. Furthermore, the participation of the bridging (H_B) and terminal (H_T) hydrogen 1s orbitals is fully compatible with the corresponding orbital localization of the SW calculation. H_T 1s AOs do not contribute to molecular orbitals with π symmetry because they lie in (1e, $1t_1$) or close to ($2t_2$) a nodal surface while H_B 1s AOs form roughly 50 percent of their character [16].

In the light of the above discussion we infer from our DV results the presence of strong π and relatively weak σ metal–ligand interaction. Furthermore, from the ordering $2t_2 < 1e$ were are lead to deduce a significant amount of ligand–ligand π interaction.

TABLE II. Comparison of Calculated Transition State Orbital Energies and Experimental Ionization Potentials for $Zr(BH_4)_4$ (Energies in eV)

Orbital	exp[a]	DV[b]	SW[c]	SW[c,d]	STO-DV[a]	STO-DV[a,d]
$1t_1$	11.6	12.4	13.9	12.4	9.7	12.4
$3t_2$		12.4	14.3	12.8	10.8	13.5
$2a_1$	12.7	12.7	14.6	13.1	11.1	13.8
1e	13.4	13.8	15.5	14.0	13.2[e]	15.9[e]
$2t_2$	13.8	14.2	15.7	14.2	11.7[e]	14.4[e]
$1t_2$	18.3	18.8	19.5	18.0	16.0	18.7
$1a_1$	19.4	19.7	20.3	18.8	17.0	19.7

[a]Ref. 2. [b]This work. [c]Ref. 1. [d]Energies shifted to adjust at the lowest calculated ionization potential of this work ($1t_1$). [e]In ref. 2 orbitals $2t_2$ and 1e have been assigned in reverse order.

In Table II we compare the experimental ionization potentials [2, 16] to transition state energies [12] of various Xα calculations [1, 2]. The specific choice of muffin-tin parameters in the SW calculation has lead to somewhat disappointing absolute agreement with experiment. Relative spacings, however, are very well reproduced, as may be seen from the values after adjustment at the lowest ionization energy of the present DV calculation to compensate for the effect of the muffin-tin potential (see Table II). The results from the present muffin-tin free DV calculation with its optimized basis set show very satisfactory agreement with experiment. To reduce the computational effort, transition state calculations were performed only for the crucial orbitals $2t_2$ and 1e. All other values have been estimated by applying the same shift to the ground state orbital energies. This seemed justified since the corresponding relaxation shift was shown to be quite uniform in $M(BH_4)_4$ spectra [1]. Let us finally mention that good agreement of the present results could only be obtained by employing self-consistently adjusted free ion basis functions in the transition state calculations. This feature is a significant advantage of the present DV methodology (see Section 2) and may be the reason behind the drastic improvement of the absolute values for the ionization potentials compared to the previous STO-DV calculation [2] (see Table II).

3.2. *$U(BH_4)_4$ – Comparison of Nonrelativistic and Fully Relativistic Calculations*

The level spectrum of the nonrelativistic and the fully relativistic Xα-DV calculation of $U(BH_4)_4$ seem to be very different at first glance (see Table III), since in the relativistic case we find double-valued symmetry representations, more symmetry allowed interactions, and additional splitting and mixing of orbitals caused by spin–orbit interaction. However, from perturbation theory we expect the latter effect to be of crucial importance only for the highly localized U 5f ligand-field manifold $3a_1$, $4t_2$, $2t_1$.

Starting from below (see Table III) we are able to directly relate the s-like ligand-derived orbitals due to their energetic and spatial characteristics: $1a_1 \rightarrow 1\Gamma_6$ and $1t_2 \rightarrow 1\Gamma_7 + 1\Gamma_8$. The relativistic contraction of the U 6p orbitals makes them less suited for bonding interaction with the B 2s AOs and thus ensues their reduced contribution to the orbitals Γ_7 and Γ_8, an effect already noticed in the quasirelativistic SW calculation [1]. There, however, the spin-orbit induced splitting of these levels had been somewhat overestimated (DV: 0.51 eV vs. SW: 0.70 eV).

The next five nonrelativistic levels 1e to $3t_2$ correspond to the next eight levels $2\Gamma_7$ to $5\Gamma_8$ in the relativistic calculation. They are predominantly B 2p and H 1s in character and constitute the well-known p-like ligand-derived manifold that is primarily responsible for the metal ligand bonding [1, 2]. Close inspection of Table III reveals that a more detailed correspondence may be set up. From the energy as well as from the almost identical atomic composition the levels 1e and $2t_2$ may be connected to their relativistic partners $2\Gamma_7$, $2\Gamma_8$, and $3\Gamma_8$, their localization being approximately 10% metal 6d, 35% boron 2p and 50% bridging hydrogen 1s in both calculations. The estimated spin-orbit splitting of the $2t_2$ level is only 0.27 eV which, although almost identical to the splitting of the orbitals $2\Gamma_7$ and $3\Gamma_8$,

TABLE III. DV-Xα Ground State Molecular Orbital Energies (in eV) and Orbital Population Analysis[a] for $U(BH_4)_4$. Comparison of Nonrelativistic and Relativistic Results

Nonrelativistic									Relativistic[b]									
Orbital	Energy	U[c]			B		H_B	H_T	Orbital	Energy	U[c]				B		H_B	H_T
		6p	6d	5f	2s	2p	1s	1s			6p	6d	5f	7s	2s	2p	1s	1s
									$7\Gamma_8$	−5.07			0.91			0.07	0.01	
									$5\Gamma_6$	−5.23			0.90			0.07	0.03	
$2t_1$[d]	−7.30			0.82		0.10	0.08		$4\Gamma_7$	−5.39		0.01	0.96				0.01	
$4t_2$[d]	· 7.77			0.95		0.01	0.01	0.02	$6\Gamma_8$[d]	−6.08		0.01	0.95			0.02	0.02	
$3a_1$[d]	−7.89			0.93			0.04	0.02	$4\Gamma_6$[d]	−6.19		0.02	0.91			0.02	0.05	
									$5\Gamma_8$	−9.48	0.01	0.02			0.04	0.53	0.03	0.38
$3t_2$	−9.20	0.04		0.03	0.01	0.48	0.11	0.34	$3\Gamma_7$	−9.61		0.02			0.05	0.51	0.01	0.40
$2a_1$	−9.93			0.04	0.06	0.50		0.41	$3\Gamma_6$	−9.87		0.02			0.10	0.45		0.42
									$4\Gamma_8$	−10.14			0.09			0.39	0.53	
$1t_1$	−10.23		0.18			0.35	0.47		$2\Gamma_6$	−10.15			0.09			0.38	0.53	
									$3\Gamma_8$	−10.78		0.11				0.39	0.50	
$2t_2$	−10.63	0.01	0.07		0.01	0.36	0.49	0.05	$2\Gamma_8$	−10.89		0.09				0.32	0.56	0.01
$1e$	−10.64		0.10			0.39	0.51		$2\Gamma_7$	−11.02		0.08				0.31	0.60	
									$1\Gamma_8$	−15.26	0.07	0.04			0.43	0.04	0.39	0.05
$1t_2$	−15.10	0.12	0.04		0.37	0.01	0.39	0.08	$1\Gamma_7$	−15.77	0.01	0.04			0.44	0.06	0.42	0.05
$1a_1$	−16.81				0.38	0.09	0.52	0.06	$1\Gamma_6$	−16.68				0.02	0.40	0.09	0.46	0.03

[a] Only populations larger than 0.01 are listed. [b] Sum of atomic contributions for $j = l \pm ½$. [c] The populations of U 7s (in the nonrelativistic case) and of U 7p AOs in all valence levels are negligible. [e] Highest occupied orbitals. Each of these levels is occupied with one electron as a result of spin or momentum polarization showing an exchange splitting of roughly 1.5 eV for the nonrelativistic and 1.2 eV for the relativistic U 5f manifold. All orbitals below are completely filled, exchange splitting is negligible there.

prevents a direct correlation with relativistic orbitals by perturbation theoretical arguments alone. In any case, it is interesting to note that the levels 1e and $2t_2$ are now virtually degenerate, a fact that is consistent with reduced ligand–ligand interaction due to the increased metal ligand distance.

The remaining orbitals of the nonrelativistic p-like manifold may be individually related to relativistic levels. The $1t_1$ level splits into the orbitals $2\Gamma_6$ and $4\Gamma_8$ with its U 5f localization halved, however. (We will come back to a discussion of this observation later on.) Both symmetry arguments and the involvement of terminal hydrogen 1s AOs prompt the identification of $2a_1$ with $3\Gamma_6$ and of $3t_2$ with $3\Gamma_7$ and $5\Gamma_8$, respectively. Again, we note a reduced U 5f contribution to these relativistic orbitals.

If we take the contribution of bridging *versus* terminal hydrogen 1s atomic orbitals as a measure of π *versus* σ bonding character of an orbital, and if we accept the metal localization of a ligand-derived orbital as a measure of its metal–ligand bonding capability, we may state a clear dominance of π over σ bonding. This statement holds both for the nonrelativistic (1e, $2t_2$, $1t_1$ *vs.* $2a_1$, $3t_2$) and the corresponding relativistic calculation and confirms the conclusions drawn from the quasirelativistic SW results [1, 16]. The energy separation, π bonding below σ bonding orbitals, becomes even clearer in the present muffin-tin free DV calculation. In the quasirelativistic SW calculation [1] the $2a_1$ level has been found 0.30 eV above the $1t_1$ orbital. The ordering $1t_1 < 2a_1$ had been suspected as a muffin-tin artifact since the corresponding energy separation turned out to be rather sensitive to the choice of the muffin-tin radii [3].

The width of the p-like manifold $2\Gamma_7$ to $5\Gamma_8$ (1.54 eV) agrees quite well with the corresponding quasirelativistic SW value (0.98 eV) if the additional broadening due to spin–orbit interaction (0.50 eV) is taken into account [1]. Comparison with experiment is hampered by the low resolution of the corresponding second band in the PE spectrum [16]. As a lower limit for the above defined width we may take the separation between the maxima characterizing the high energy and low energy shoulders of this band (1.1 eV). Experimental resolution is better for the third band in the PE spectrum [16] where two maxima may be identified, 1.3 eV apart. The width of the B 2s manifold $1\Gamma_6$ to $1\Gamma_8$ (1.42 eV) is in excellent agreement with experiment, substantially improved over the value of the SW study (0.49 eV). The gap between s- and p-like levels is almost identical in both calculations (DV: 4.24 eV; SW: 4.27 eV; experiment: 4.8 eV [16]). To judge the present calculation in absolute terms, a representative transition calculation was performed for the $5\Gamma_8$ level (onset of p-like manifold). The calculated ionization energy of 11.9 eV agrees very well with the maximum of the first shoulder in the corresponding PE band at 11.9 eV. Again we note a substantial improvement over the value of 13.8 eV from the SW calculation.

After the discussion of the completely filled ligand-derived levels we now turn to the quasiatomic U 5f crystal field levels which hold the two remaining electrons of the formal configuration U $5f^2$. However, me must refrain from setting up unique connection between the nonrelativistic levels $3a_1$ to $2t_1$ and their relativistic counterparts $4\Gamma_6$ to $7\Gamma_8$ since the crystal field (CF) splitting is comparable to that induced by spin–orbit (SO) interaction. This is known both from an analysis [18] of the optical spectrum of $U(BD_4)_4$ (CF: 0.56 eV: SO: 0.77 eV) and from the quasirelativistic SW calculation (CF: 0.91 eV; SO: 0.76 eV). The quasiatomic SO splitting quoted here has been calculated from the usual SO constant ζ [18] according to the well-known relation: $\Delta E = \zeta\,(2l + 1)/2$.

In our fully relativistic DV calculation we find a largely spin–orbit dominated pattern: $j = 5/2$ levels lying 0.69 eV below $j = 7/2$ levels. The U 5f atomic orbital character is almost purely $f_{5/2}$ for the levels $4\Gamma_6$ and $6\Gamma_8$, and almost purely $f_{7/2}$ for the remaining levels $4\Gamma_7$, $5\Gamma_6$ and $7\Gamma_8$. Some mixing does occur in the two Γ_6 orbitals (about 20% of the other j value). If one analyzes [19] the splitting pattern of the six levels of the relativistic ligand field manifold using a model Hamiltonian which includes the usual crystal field terms and spin–orbit interaction, one obtains the following three quasirelativistic levels underlying the present DV results: $2a_1$ at −5.99 eV, $4t_2$ at −5.73 eV, $2t_1$ at −5.31 eV [19]. The resulting values for the CF and quasi-atomic SO splitting are 0.68 eV and 0.80 eV, respectively, in good agreement with experiment [18]. It should be mentioned that not only the splitting, but also the ordering of the one-electron ligand field levels concurs with that extracted from experiment [1, 18, 19].

Most conspicuous in Table III is the lower energetic position of the nonrelativistic U 5f manifold by 2.0 eV compared to the relativistic 5f manifold, e.g. in their quasirelativistic form just described (see also Table III). Concomitant with the smaller energetic separation of the nonrelativistic 5f levels from the p-like ligand derived orbitals we find a stronger covalent mixing between these two manifolds. This is especially noticeable in the higher f covalency contribution of the $1t_1$ orbital and the reduced localization of its antibonding partner $2t_1$ compared to the corresponding relativistic orbitals. Similar effects have been found and rationalized in a comparative study of nonrelativistic and quasirelativistic Xα-SW calculations of uranocene, $U(C_8H_8)_2$ [20]. We will come back to this topic in the following section.

TABLE IV. Population Analysis[a] and Atomic Charges for the Molecules M(BH$_4$)$_4$, M = Zr, U

Zr(BH$_4$)$_4$		U(BH$_4$)$_4$				
Orbital		Orbital	nonrel.	relativ.[b]		(j)
Zr 4d	1.95	U 6d	1.11	1.30	0.56	(3/2)
					0.74	(5/2)
4f	0.00	5f	3.27	2.43	1.83	(5/2)
					0.60	(7/2)
5s	0.04	7s	−0.11	0.11		
		7p	−0.18	−0.12	−0.01	(1/2)
					−0.11	(3/2)
charge	+2.02	charge	+1.93	+2.25		
B 2s	0.89	B 2s	0.88	0.98		
2p	2.61	2p	2.55	2.60	0.88	(1/2)
					1.72	(3/2)
charge	−0.50	charge	−0.42	−0.58		
H$_T$ 1s	0.92	H$_T$ 1s	0.95	0.91		
charge	+0.08	charge	+0.05	+0.09		
H$_B$ 1s	1.03	H$_B$ 1s	1.04	1.02		
charge	−0.03	charge	−0.04	−0.02		

[a] The completely filled core-like orbitals Zr 3s, 4p and U 6p are not listed. [b] Also given are the populations of the various components for $j = 1 \pm ½$.

3.3. Comparison of Bonding Characteristics in Zr(BH$_4$)$_4$ and U(BH$_4$)$_4$ – Atomic Orbital Populations

It is quite instructive to examine the ground state atomic orbital populations obtained in the present DV-Xα calculations (see Table IV). Starting with a comparison of the transition metal and the actinide borohydride (relativistic treatment), we find the charge of both tetravalent metal atoms substantially reduced from their nominal value (Zr: +2.02; U: +2.25). In a completely ionic compound the metal configuration would be Zr^{4+} [4d^{0}4f^{0}5s^0] and U^{4+}-[6d^{0}5f^{2}7s^{0}7p^0]. As a measure of the covalent character of the bonding we may take the metal population of the various ligand-derived orbitals [1]. It is then clear from Tables I, III and IV that a reasonable amount of covalent bonding is present in both molecules, mainly through the p-like ligand-derived orbitals. We observe a strong metal d orbital participation, though noticeably less in the actinide (6d: 1.30) than in the transition metal borate (4d: 1.95). On the other hand, the Zr 4f orbitals do not accumulate any charge while the U 5f orbitals are populated with 2.43 electrons (of which only the excess over the f^2 configuration should be counted towards covalency).

A quantitative comparison of the populations with the corresponding SW partial-wave occupations [1] is not meaningful because of the rather different methodological basis of both quantities. However, the same trends can be identified in both calculations: more d orbital bonding in the transition metal than in the actinide compound, significant covalent participation of the f orbitals in the uranium complex. Adding the d and f orbital contributions to the ligand p-like manifold separately (Table III), we find a relation f:d = 0.50 for U(BH$_4$)$_4$, the corresponding SW value being 0.60 [1]. The metal s valence orbitals (Zr 5s, U 7s) can be seen to play only a subordinate role in the bonding of both complexes. Inspection of Tables I and III confirms the well-known fact [1, 2] that on the ligand side bonding is dominated by the B 2p orbitals with important contributions from the bridging hydrogen atoms via the π bonding orbitals 2t$_2$ and 1e [1, 17]. The bridging hydrogen atoms acquire a small negative charge and more electron density than the terminal hydrogen atoms emphasizing their mediating role in the metal–ligand bonding.

The most obvious difference in the level ordering of the transition metal and the actinide compound is the relatively lower position of the 1t$_1$ orbital (2Γ_6 and 4Γ_8) within the p-like manifold of the uranium complex. This is certainly due to the participation of the U 5f orbitals as may be ensured by a comparison of nonrelativistic and relativistic results. The larger f population in the non-relativistic case correlates with energy separation relative to the highest orbital of the p-like manifold (1t$_1$ to 3t$_2$: 1.03 eV; 2Γ_6 to 5Γ_8: 0.67 eV).

This observation leads us finally to a discussion of relativistic effects in the DV-Xα description of the electronic structure of U(BH$_4$)$_4$. Just as in a previous Xα-SW study [20] of uranocene, U(C$_8$H$_8$)$_2$, we find the relativistic Xα description of the complex more ionic than the nonrelativistic treatment (see Table IV). This can be traced to a change in the U 6d and 5f populations. The increase in the 6d population of the relativistic case by 0.19 electrons is overcompensated by a loss of 0.84 f electrons. The corresponding values for uranocene are rather similar [20]: Δd = 0.21 and Δf = −0.63.

It is a generally held view [21] that s and p orbitals of heavy elements are contracted when relativistic effects are taken into account whereas d and f orbitals are expanded due to increased inner shielding of the nuclear charge. Their participation in metal–ligand bonding should change accordingly. In Xα calculations, changes in the populations of s, p and d orbitals of uranium compounds show the expected trend indeed, not however the change of the f orbital occupation (see Table IV and ref. 20).

This counterintuitive finding has been rationalized [20] as an artifact of the Xα model in the nonrelativistic description of the uranium atom. The Xα model requires filling levels strictly from below in the ground state, possibly entailing partial occupations only in the highest degenerate levels. In the nonrelativistic Xα model ground state of the uranium atom electronic charge has to be redistributed from the 7s into the lower lying 5f level until their energies match due to the increased coulomb repulsion of the strongly localized f orbitals. Compared to the relativistic Xα ground state U 5f$^{3.41}$ 6d$^{0.59}$ 7s^2 (where only a minor redistribution of electrons from the 6d into the 5f level is necessary compared to the experimental configuration 5f^3 6d^1 7s^2) one finds [20] the non-relativistic configuration 5f$^{4.66}$ 6d^0 7s$^{1.34}$. The 5f orbital energy in the nonrelativistic case is somewhat lower, the 6d orbital energy somewhat higher than in the relativistic description. In the complex these orbitals interact with lower lying ligand orbitals (the p-like manifold in the case of tetrahydroborate). From the perturbation theory one deduces a stronger covalent 5f interaction in the nonrelativistic case due to more favourable energy denominators. The lower energy of the nonrelativistic U 5f level shows up even in the energy of the corresponding molecular orbitals of the complex. An analogous argument explains the observed opposite population changes of the 6d orbitals.

From the previous investigation of uranocene [20] and the present study of uranium borohydride it is obvious that nonrelativistic Xα calculations of actinide complexes [22–24] produce a distorted description of the electronic structure.

4. Conclusions

The results of the present muffin-tin free DV-Xα molecular orbital study on the tetrakis tetrahydroborates of zirconium and uranium may be summarized as follows:

The findings of a previous Xα-SW investigation on metal tetraborohydrides have essentially been confirmed. The metal–ligand bonding is characterized by an unusually strong π interaction due to the BH_4 ligands.

The calculated ionization potentials of this DV study show noticeably improved agreement with experiment. For $Zr(BH_4)_4$, the order of the two most strongly bonding orbitals is $2t_2 < 1e$, indicative for substantial ligand–ligand interaction and in agreement with the interpretation of the PE spectrum derived from the SW calculation, but at variance with the PE assignment of the earlier STO-DV-Xα investigation.

Nonrelativistic treatment of the uranium complex leads to an overestimation of the covalent ligand metal interaction due to a pecularity of the Xα method. This effect shows up in exaggerated U 5f and in underestimated U 6d participation in the bonding. For a proper Xα description of the electronic structure of actinide complexes a calculational procedure is mandatory which includes relativistic effects.

A more detailed discussion of questions associated with the 5f crystal field manifold of tetrahedral actinide compounds will be given in a future communication [19].

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