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**ELECTRONIC STRUCTURE AND CHEMISTRY
OF THE HEAVIEST ELEMENTS**

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Electronic Structure and Chemistry of the Heaviest Elements

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Electronic structure and chemistry of the heaviest elements

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I. Introduction

The periodic system of the elements, which was introduced by Mendeleev more than 100 years ago, serves as the basic ordering scheme for chemical elements and is the most important and useful tool to predict in general their chemical behavior. Within the last several years the periodic table has been considerably extended. Using complete fusion reactions, the heaviest elements up to atomic number 112 have been produced [1,2]. Nuclear theory predicts that element 112 might not be the last one and that even heavier elements may exist around atomic number 114 and beyond. As the actinide series ends with element 103, all elements beyond are called transactinides.

Of, at least, equal importance to the production of new elements is the investigation of their physical and chemical properties, since it is extremely valuable to establish whether the basic concept of the periodic system is still valid in the area where relativistic effects become increasingly important. Under intensive study are presently elements 104 through 112 constituting the last existing transition element series. Since in these elements the filling of the $6d$ -shell takes place, they are expected to exhibit chemical properties analogous to those of the $4d$ and $5d$ transition elements. The task has therefore been to prove experimentally and theoretically whether their properties are typical of the lighter homologs in the corresponding groups, or whether they deviate from the trends found within the lighter homologs due to strong relativistic effects on their electronic shells.

Until now, experimental investigations of chemical properties of the transactinides were possible only for isotopes with half-lives of the order of 10 seconds and more. These elements are 104, rutherfordium (Rf), 105, dubnium (Db) and 106, seaborgium (Sg) [3-13]. Element 107, bohrium (Bh), and 108, hassium (Hs), were predicted to have some isotopes with a half-life of the order

of few seconds, thus indicating the feasibility of the chemical experiments as well [3b]. For the heavier elements, future will show if they can be investigated chemically.¹

Due to short half-lives and low production rates of these elements, experimental investigations of their properties are connected with large difficulties. To overcome these problems, special "fast-chemistry" techniques of the one-atom-at-a-time chemistry have been developed. They are based on the principle of the chromatographic separation, which has an advantage over other methods, since each of the few available atoms experiences many adsorption-desorption cycles thus ensuring a statistical chemical behavior. The experiments are subdivided into two large groups: gas-phase chromatography experiments [4–9] studying volatility of the heavy elements and their compounds, and liquid chromatography ones [10–12] studying the complex formation in aqueous solutions.

Results of these chemical experiments [4–12] provided strong evidence that the actinide series ends at Lr and a new series begins with element 104. Rf was found to be a homolog of the group 4 elements, Zr and Hf, and Db a homolog of the group 5 elements, Nb and Ta. Very recently, element 106(Sg) was shown to behave similar to Mo and W, so that its place in group 6 was confirmed [13]. Reviews covering the experimental research in this area can be found in refs. [14–25] and in the article of J. V. Kratz in this book.

The results of these experiments have, however, revealed that measured properties were often different from those expected from straightforward extrapolations within the groups, and trends were even reversed. The need to find an explanation of these phenomena, as well as the complexity and high costs of the experiments on the transactinides have made theoretical investigations and predictions highly desirable.

First predictions of chemical properties of the superheavy elements based on results of relativistic atomic Dirac-Fock (DF) and Dirac-Slater (DS) calculations, different qualitative theories, and general knowledge about the periodic system were made more than 25 years ago [26–38]. Trends in fundamental properties such as ionization potentials, ionic, atomic and metallic radii, electronic configurations, stabilities of oxidation states, etc. of elements belonging to the transition $6d$, $7d$ and $8d$ series have been established leading to conclusions about a similarity of the transactinides with the lighter homologs of the $4d$ and $5d$ series. Reviews covering this area can be found in

¹ Because the names of most of these elements were not internationally agreed until 1997, sometimes different names were used. This is especially true for element 105, dubnium (Db), which in most publications until the end of 1997 was called hahnium (Ha). In this review, the name hahnium is still used in all the figures borrowed from the previous publications.

refs. [14,37,38]. Since then, new values of the atomic properties of some transactinides have been derived from more accurate multiconfiguration Dirac-Fock (MCDF) [39–44] and quite recently from DF coupled-cluster (CC) calculations [84–86]. Theoretical investigations of molecular properties of the transactinides, except a very few publications [45–48], have been started only in the beginning of the nineties [49–68] initiated by a growing number of questions connected with the experimental research. Results of the theoretical studies of molecular properties, as well as of the recent studies of atomic properties for elements beyond Lr will be overviewed in this publication, though earlier reviews can be found in refs. [69a,b].

II. Relativistic effects on atomic properties of the transactinides

Increasing proportionally with respect to Z^2 for atomic electronic shells, relativistic effects are known to be responsible for stabilization of the s and p orbitals and their spatial contraction, and, as an indirect relativistic effect, destabilization and expansion of the (outer) d and f orbitals. In the $5d$ elements, such changes in the valence $6s$ and $5d$ orbitals result in quantitative and qualitative alterations in properties of their compounds [92–99]. Much larger changes in the energy and spatial distribution of the valence $7s$, $7p$ and $6d$ electrons in the transactinides might result in larger changes in properties, leading to deviations from the known trends. Among these properties are electronic configurations, ionization potentials (IP), atomic/ionic radii (AR/IR), oxidation states (redox potentials), complexing ability, etc..

A. *Relativistic methods to calculate the electronic structure of heavy atoms and ions*

The necessity to use the Dirac equation for an adequate description of the electronic structure of heavy atoms and molecules has been recognized since long and the corresponding relativistic atomic and molecular codes based on the DF approximation have been developed. An adequate description of the instantaneous electron-electron interaction in the DF schemes, called the electron correlation is, nevertheless, a serious methodical problem, though for heavy elements correlation effects are known to be as large as relativistic effects. The approximations, which are presently used to describe the correlation effects are the configuration interaction (CI), many-body perturbation theory (MBPT) and the CC technique.

Early calculations of the electronic structure of heavy element atoms and ions have been performed by Mann, Waber, Desclaux and co-workers using the

single-configuration DF method [26,29,36,70a] and by Fricke, Greiner and co-workers using the local-density DS model [27,28,31,37,38,70b]. Results and their application to the interpretation of chemical properties have been summarized in refs. [37, 38]. (The full list of atomic calculations up to 1985 can be found in ref. [71]). The accuracy of the methods and their application are shown in Table 1.

Table 1
Atomic codes used for calculations of the transactinides

Method	Atoms	Properties	Error, eV ^a	Reference
DS	104-172	ground state, IP(I)	$\sim 0.2-0.8$	[37,38]
DF	1-172	ground state, IP(I), $R_{\max}$	$IP < \sim 0.8$	[29,36]
MCDF	103-105	EE, multiple IP	$EE \sim 0.25$	[39-43]
		$R_{\max}$, IR	$IP \sim 0.4$	
DF+CCSD	103,104, 111-116, 118, 121-122	ground and 1^{st} exc. states EE, IP(I)	$EE, IP < 0.1$	[84-88]

^a EE - excitation energies.

Starting in 1980, MCDF calculations of Desclaux, Fricke, Johnson, and Glebov *et al.* [39-42] for Lr, Rf and Db appeared (Table 1) showing in some cases significantly different results than those, which were expected on the basis of a straightforward extrapolation of the periodic table, or from the DS and DF calculations. The MCDF method is known to take into account most of the correlation effects while retaining only a reasonable number of configurations [72].

Another method, successfully treating correlation effects in many-electron systems is the relativistic many-body perturbation theory [73]. The method is, however, more suitable for highly charged ions (where few terms of the perturbation series suffice) [74-77], but less for neutral atoms (where higher orders of the series are non-negligible). No calculations of the transactinide atoms and ions have been reported.

The drawbacks of the MBPT method are partially eliminated in the coupled-cluster (CC) formalism [78-83], an all-order method, where infinite subclasses of contributions are summed [79a,b]. The atomic CC method in its CCSD (single and double excitations) approximation developed by Kaldor and Eliav [79b] is the most accurate at the moment for a large variety of systems. The

method takes into account most of the dynamic correlations, omitted from MCDF, and a core polarization. At present, it is limited to one and two particle valence sectors of the Fock space, i. e., it can only treat the states which can be reached from a closed shell by adding or removing no more than two electrons. The computational costs are very high. The accuracy of the method is indicated in Table 1. The CCSD method has been applied to calculations of the electronic structure of heavy elements 103, 104, and 111–112 [84, 85], and superheavy elements 113–118 [85c, 87, 88] and 121–122 [87a]. For the practical need of the experimental research, however, the MCDF calculations are presently of more use since they can provide multiple IP needed, e.g., to estimate redox potentials of the heavy elements in aqueous solutions, as well as IR important for their chemical separation.

B. The electronic structure of the transactinide atoms and ions

Electronic configurations. Relativistic changes in energies of the $7s$, $7p$ and $6d$ electrons of the $6d$ elements might results in the stabilities of electronic configurations different from those expected by analogy with the lighter homologs. Lr was the first element where a strong relativistic stabilization of the $7p_{1/2}$ orbital was supposed to result in an unusual ground state. This state, $7s^27p$, was first proposed by Mann [29c] and later by Brewer [89], though the DF calculations of Desclaux [36] predicted $7s^26d$.

Later, Desclaux and Fricke [39], using the MCDF method, have shown that spin-orbit stabilization plays a dominant role in Lr, so that the ground-state electronic configuration is indeed $7s^27p$ ($^2P_{1/2}$) in contrast to the earlier expected $7s^26d$ assumed by analogy with Lu. In these calculations, the energy difference between the $(n-1)d$ and np configurations of Y, La and Lu was about 0.3 eV lower compared to the experimental value. The calculated energy difference for Lr was corrected by this value which resulted in the $7s^27p$ ground-state. The first excited state $7s^26d$ ($J = 3/2$) was found to be at about $(1.5 \pm 1)10^3 \text{ cm}^{-1}$.

Recently, CCSD calculations [86] for Lr confirmed the $7s^27p$ ground state obtained in the MCDF calculations [39]. The next excited state, $7s^26d_{3/2}$ ($^2D_{3/2}$), is found to be about 0.16 eV higher in energy, which is in good agreement with the corrected value of 0.186 eV from the MCDF calculations [39]. The $7s^27p_{1/2}$ configuration proved to be a result of the relativistic stabilization of the $^2P_{1/2}$ state.

For Rf, MCDF calculations [40, 41] have also given a ground-state, which is different from that expected from the periodic table. This state was shown to be $J = 2$ consisting of $6d7s^27p_{1/2}$ (80%), with the first excited state $6d^27s^2$

(95%) at 0.5 eV [40] or 0.24 eV [41] higher in energy. The $7s^27p^2$ electronic configuration, proposed in ref. [16] as the ground state, turned out to be 2.9 eV above the ground state.

Recent calculations [84] using the CCSD method have, however, given a different electronic configuration for Rf than the one obtained by the MCDF method, but in agreement with the early DF and DS predictions [36–38]: $7s^26d^2$ ($^3F_2$). The $7s^27p6d$ ($^3D_2$) state was found to lie about 0.30 eV above the ground state. The difference between the MCDF and CCSD calculations was explained by the dynamic correlation effects, requiring virtual orbitals with the quantum number l up to 6 (the MCDF calculations have taken into account the correlation of only outer four electrons). The Breit interaction was shown to have a large effect on total energies, but a very small effect on correlation and transition energies in the outer shells.

For Db, the MCDF calculations [42] have given $6d^37s^2$ as the ground state in accordance with the earlier predictions [37, 38]. The relativistic stabilization of the $7p_{1/2}$ orbital manifests itself in the first excited $6d^37s7p$ configuration lying at 1.9 eV higher in energy. The $6d^47s$ configuration, which was expected earlier to be the next excited state, turned out to be 2.0 eV above the ground state. Preliminary MCDF calculations [90] have shown a similar situation for Sg: the ground state is $6d^47s^2$ and the first excited state is $6d^37s^27p$, located 1.64 eV higher in energy. Results of the recent MCDF and CCSD calculations for elements 104 through 106 are summarized in Table 2.

Table 2
Results of the atomic calculations for Rf, Db and Sg

Property	Rf		Db	Sg
	MCDF ^{a,b}	CCSD ^c	MCDF ^d	MCDF ^e
ground state	$6d7s^27p$	$6d^27s^2$	$6d^37s^2$	$6d^47s^2$
exc. state	$6d^27s^2$	$6d7s^27p$	$6d^37s7p$	$6d^37s^27p$
EE ^f , eV	0.5 ^b ; 0.24 ^c	0.30	1.90	1.64
IP(I), eV	6.50	6.01	6.89	7.10
Σ IP(max), eV	76.80	-	126.38	-

^a Ref. [40]; ^b ref. [41]; ^c ref. [84]; ^d ref. [42]; ^e ref. [90]; ^f EE - excitation energy.

For element 111, CCSD calculations [85a] have shown that in contrast to the lighter group 11 elements, the atomic ground state is $6d^97s^2$ ($^2D_{5/2}$); the $^2D_{3/2}$ state is higher by 2.69 eV, and the $6d^{10}7s$ configuration lies 2.95 eV above the $^2D_{5/2}$. The reversal is ascribed to relativistic effects. These results are very close to the relativistic Hartree-Fock-Slater (HFS) calculations of Keller *et al.* [30]. For element 112, CCSD calculations [85b] have confirmed the $6d^{10}7s^2$ ground

state. For element 113, a recent CCSD result [85c] was the $6d^{10}7s^27p_{1/2}$ ($^2P_{1/2}$) as the ground state in agreement with the old DFS calculations [37].

In summary, the relativistic stabilization of the ns electrons is observed in the $5d$ elements in contrast to the $4d$ ones (the change of the configuration from d^m5s to $5d^{m-1}6s^2$, see Table 3) [28, 37, 38, 91, 92]. Nevertheless, in the case of Au, the tendency to fill the d -shell is still stronger than the relativistic stabilization of the $6s^2$ pair, so that the ground state is $5d^{10}6s$. The stabilizing effect of the $d^m s^2$ configuration becomes even larger in the next period, i.e. for the $6d$ elements, because the $7s$ electrons drop relatively deep into the atom. Thus, they feel a very strong potential near the nucleus, whereas the $6d$ electrons are shielded more strongly by the $5f$ electrons. Such a strong relativistic stabilization of the $7s$ electrons of the transactinides results in the stabilization of the $7s^2$ pair over the entire $6d$ -transactinide series, so that in the case of element 111, the relativistic stabilization of the $7s^2$ pair causes the $6d^97s^2$ state to be the most stable [30, 85a].

Table 3

Ground and first ionized states for group 4-6 elements. (From. ref. [69a]).

	Group 4			Group 5			Group 6		
	Zr	Hf	Rf	Nb	Ta	Db	Mo	W	Sg
M	$4d^25s^2$	$5d^26s^2$	$6d^27s^2$	$4d^45s$	$5d^36s^2$	$6d^37s^2$	$4d^55s$	$5d^46s^2$	$6d^47s^2$
M ⁺	$4d^25s$	$5d6s^2$	$6d7s^2$	$4d^4$	$5d^36s$	$6d^27s^2$	$4d^5$	$5d^46s$	$6d^37s^2$

The stabilization of the $7s^2$ pair with increasing Z is particularly seen for the +1 ionized state of the transactinides in contrast to their $5d$ analogs (with some exceptions like Hf⁺) having the $(n-1)d^m ns$ configurations, as it is shown for Rf⁺, Db⁺, Sg⁺ (Table 3), 111⁺, and 112⁺ [40–42, 85, 90].

From the chemical point of view, the relativistic stabilization of the $7p_{1/2}$ and $7s^2$ electrons was a reason to think about enhanced stability of lower oxidation states at the beginning of the transactinide series. This question, as well as those where chemical properties (e.g., volatility of metals) can be influenced by the changes in electronic configurations will be addressed further, in sections III and V.A.

Orbital energies and ionization potentials. The influence of relativistic effects on the energies of the valence electrons and IPs has been analyzed in ref. [57] on the basis of HFS and DS atomic calculations, as well as on the HF and DF data of ref. [36]. As an example, nonrelativistic and relativistic binding energies of the valence ns and $(n-1)d$ electrons for group 5 elements and Pa are shown in Fig. 1. The ratio of the relativistic DS to the nonrelativistic HFS eigenvalues for the valence electrons of Nb, Ta, and Db are given in Table 4.

These data evidently show the opposite action of the relativistic and shell

Fig. 1. Binding energies of the valence electrons for Nb, Ta, and element 105 (Ha) as a result of the DF relativistic and HF nonrelativistic calculations [36]. (From ref. [57]).

effects for the valence electrons with increasing atomic number (the relativistic stabilization of the ns and destabilization of the $(n-1)d$ orbitals in contrast to the nonrelativistic destabilization of the ns and stabilization of the $(n-1)d$ orbitals), especially in the case of the transactinides, where the nonrelativistic description of the wave functions would result in just the opposite trend in properties within the group.

Table 4

Ratio of relativistic (DS) to nonrelativistic (HFS) $R_{\max}$ and eigenvalues (E) for the valence electrons of Nb, Ta, and Db. (From ref. [57]).

Atom	ns	$np_{1/2}$	$np_{3/2}$	$(n-1)d_{3/2}$	$(n-1)d_{5/2}$
E^{rel}/E^{nr}					
Nb(d^4s)	1.0715	1.0879	0.9695	0.9341	0.8762
Ta(d^3s^2)	1.1833	1.1458	0.7521	0.7543	0.6164
Db(d^3s^2)	1.5245	1.4612	0.4480	0.5514	0.3264
$R_{\max}^{rel}/R_{\max}^{nr}$					
Nb(d^4s)	0.9702	0.9660	0.9989	1.0080	1.0186
Ta(d^3s^2)	0.9089	0.9080	1.0191	1.0081	1.0453
Db(d^3s^2)	0.7945	0.7870	1.0596	1.0127	1.0962

The pseudohomolog of Db, Pa, located at the beginning of the transactinide series has much less stabilized $7s$ and $6d$ electrons than Db, having a filled $5f$ -shell and experiencing the actinide contraction (since the $7s$ orbitals are not well screened and attracted to the core). It has also the $5f$ electrons in the valence region. Therefore, the bonding made by the valence orbitals of Pa will be different from that of Db. The same effect was found for Sg with respect to U [68]. A trend in the changes of the relativistic and nonrelativistic energies of the atomic orbitals from W to Sg was found to be similar to that from Ta to Db (ref. [57] and Fig. 1). The $7s$ orbital of Sg turned out to be stabilized by 2.54 eV and contracted by about 0.34 Å by relativistic effects.

First and multiple DS IP for elements 104 through 112 are given in ref. [38]. Recently, the MCDF [40,41] and CCSD [84,85] values of IP have been provided for elements Rf, Db, and 111 through 113. The MCDF multiple IP, radii of maximum radial charge density ($R_{\max}$) and IR for the group 4 and 5 elements are given in Table 5 together with the references.

Table 5

Multiple ionization potentials (0-4+) and (0-5+), radii of maximum radial charge density ($R_{\max}$) and ionic radii (IR) for M^{4+} and M^{5+} . (From ref. [69a]).

Element	Group 4			Element	Group 5		
	Σ IP, eV ^a	$R_{\max}$, Å ^b	IR, Å ^c		Σ IP, eV ^a	$R_{\max}$, Å ^d	IR, Å ^c
Ti	91.15	0.47	0.61	V	162.64	0.44	0.54
Zr	77.29	0.62	0.72	Nb	135.05	0.59	0.64
Hf	77.50	0.63	0.71	Ta	132.03	0.60	0.64
Rf	76.80 ^b	0.71	0.79	Db	126.38 ^d	0.69	0.74

^a Ref. [101]; ^b ref. [41]; ^c ref. [102]; ^d ref. [42]

Relativistic destabilization of the $6d$ -AOs and their spin-orbit (SO) splitting result in the relativistic first and some other IPs of the transactinides being lower than the nonrelativistic ones, and they are lower than those of the analogous $5d$ -elements. Such a decrease in IP for the transition from the neutral to the maximum oxidation states in group 4 and 5 enhances the stability of the maximum oxidation states in the direction to Rf and Db, respectively (Table 5). The same would probably hold for group 6, where the MCDF calculations of the electronic structure of Sg are in progress [90].

Radial charge-density distributions and atomic/ionic radii. The DF values of $\langle r^n \rangle$ ($n = -3, -1, 1, 2, 4$, and 6) for elements up to 120 are given in ref. [36]. The MCDF $R_{\max}$ in the outermost shells for Rf and Db and AR/IR of these elements in different oxidation states estimated by normalization and extrapolation of $R_{\max}$ over the known experimental values [41,42] are given in refs. [40–42]. An analysis of the influence of relativistic effects on $R_{\max}$ of the transactinides can be found in refs. [57,67] and [68]. As an example, a relativistic

radial contraction of the $7s$ orbitals (of 20.5%) of Db is shown in Fig. 2. For Zr, Hf and Rf, the DF values of $R_{\max}(ns)$ are 3.291, 3.048 and 2.972 a.u., respectively [36]. The same is valid for the +1 oxidation state of group 4 elements [41]. Thus, due to the relativistic contraction of the ns and $np_{1/2}$ orbitals, their relativistic $R_{\max}$ decreases with increasing Z , while the nonrelativistic values show just the opposite trend. (For these orbitals relativistic and shell effects act in opposite directions). For relativistic $np_{3/2}$, $(n-1)d_{3/2}$ and $(n-1)d_{5/2}$ electrons, $R_{\max}$ increases in going down the group, with the relativistic effect enhancing the orbital effect, especially for the $(n-1)d_{5/2}$ orbitals. Due to such a decrease in $R_{\max}$ of the outer ns electrons, the AR decreases within the transition element groups (though the MCDF calculations [41] have given a larger IR(Rf) due to the outer $7p$ electron in the $6d7s^27p_{1/2}$ configuration).

Along the $6d$ -transactinide series, the ns function becomes more contracted and $R_{\max}$, as well as AR also decrease, so that their smallest values will be at element 112 [36–38]. (The $5f$ -shell contraction effect was shown to be enhanced by relativity [100]). A much smaller $R_{\max}(7s)$ for elements 111 and 112 compared to Ag, Au and Cd, Hg, respectively, was supposed to result in the smallest bond lengths 111-X and 112-X in the series MX (X - electropositive ligand) [100].

For the elements in the highest oxidation states, IR increases within the groups. Thus, the data of Table 5 show that IR(M^{4+}) and IR(M^{5+}) of the $4d$ and $5d$ elements, respectively, are almost equal due to the lanthanide contraction (of about 0.18 Å), which was shown [48] to be a mostly nonrelativistic effect. The IR of the corresponding transactinide ions are larger than those of the $5d$ elements due to the shell-structure expansion of the outer $6p_{3/2}$ orbitals enhanced by relativity. Due to the actinide contraction (of 0.30 Å), which is a mostly relativistic effect, the IR of the transactinides are smaller than the radii of the corresponding actinides. Thus, as it was concluded earlier [37,38], larger ionic and covalent radii, smaller ionization energies and close spacing of the energies of the valence orbitals of Rf and Db, compared to their lighter homologs will facilitate the stability of their maximum oxidation states and will be the basis for a rich chemistry of complex ions in solutions.

Since the strength of chemical bonding in a compound is known to be determined by energies of atomic valence shells and their spatial distribution, the opposite trends in these atomic properties of the relativistic and nonrelativistic valence ns and $np_{1/2}$ electrons with increasing Z will result in different trends in chemical bonding, stabilities of oxidation states and other molecular properties in going from the $5d$ to the $6d$ compounds, as it will be shown further on the example of various halide and oxyhalide molecules of Rf, Db and Sg in the gas phase (section IV.B) and their complexes in aqueous solutions (section V).

Fig. 2. Radial distribution of the ns valence electrons in Nb, Ta and element 105 (Ha) as a result of atomic relativistic DS calculations (full line) and HF nonrelativistic (dashed line) calculations. The dashed-dotted (mol) are relativistic calculations of the metal ions for electronic configurations obtained in the molecular DS-DV calculations for MCl_5 . (From ref. [57]).

III. Transactinide metals

Early predictions of properties of the transactinides in macroscopic quantities have been summarized in refs. [37, 38]. The metallic radii were obtained by extrapolations of comparisons of the experimental trends, as well as of the calculated trends of the radii of the outermost s and d electrons, taking into account the fact that the outer electrons become more or less itinerant conduction electrons and are distributed over the crystal. The metallic radii were shown to be smaller at the beginning of the period and somewhat larger at the end of it (see Fig. 7 in ref. [37]). For element 112, the predictions indicated that it should be distinctly a noble metal with the interatomic interaction being small in the metallic state (because both the $6d$ and $7s$ outer electron shells are filled and their ionization energies are higher than those of homologs). This will possibly lead to high volatility of it like in the noble gases.

Another important quantity of a metal which has to be known is the sublimation enthalpy, ΔH_s . This is very important not only for predicting properties of individual atoms, but also for calculating different properties of compounds, such as the enthalpy of formation, of sublimation, etc. There were several attempts to estimate the sublimation energies of the very heavy metals such, e.g., as heavy actinides using experimental data on the heats of adsorption of single atoms on a metallic surface [103, 104]. This technique is, however, not applicable to the transactinides, since it is extremely difficult to stabilize these elements in the atomic state at the temperatures above 1000 °C. Thus, for the transactinides ΔH_s have only been estimated mostly using the periodic law [15, 38].

Among heavy elements, Lr was a special subject of interest due to the (calculated) $7s^27p$ ground state [39]. This element was believed to be as volatile as other p -elements, e.g. Tl, having the $6s^26p$ ground state. First Keller [16] and then Eichler [105] used a linear correlation between ΔH_s and the atomic number of elements Al-Ga-In-Tl to estimate $\Delta H_s(p)$ for Lr as a " p "-element. The obtained value of $\Delta H_s(p)$ was 135 kJ/mol, which means that the volatility of Lr would be as high as that of the other p -elements.

$\Delta H_s(d)$ for Lr as a " d "-element was estimated [107–110] using the following relation

$$\Delta H_s = E_b - \Delta E, \quad (1)$$

where E_b is the binding energy and ΔE is the difference between electronic configurations in the metallic and gaseous states. E_b was shown [106–108] to vary smoothly with atomic number, and for the actinides to be nearly a constant value. The obtained $\Delta H_s(d)$ for Lr were 414 kJ/mol [107, 108];

351 kJ/mol [109] and 410 kJ/mol [110]. Thus, the difference between $\Delta H_s(d)$ and $\Delta H_s(p)$ was found to be ~ 4 eV, which could have been detected easily in experiments.

Attempts to separate $\text{Lr}(p)$ from the other actinides using the high-temperature gas-phase chromatography in quartz and Pt columns [4], nevertheless, failed. Lr was found to be as non-volatile as the other actinides. The results, however, did not exclude existence of $\text{Lr}(p)$. It is possible, that when interacting with the surface of the column the atom easily reaches its excited $7s^26d$ state, which is only 0.24 eV above the ground state, thus losing its "p"-character.

For Rf, ΔH_s was calculated [49] using also relation (1), with E_b being shown to have a linear dependence on the atomic number in group 4. This result has, nevertheless, been obtained for the $6d7s^27p$ ground state shown by the MCDF calculations [40]. After recent CCSD calculations [84] giving the $6d^27s^2$ configuration as the most stable, these values should be reconsidered.

Another empirical approach to estimate ΔH_s for the transactinides was suggested by Eichler [104, 112]. He used a linear correlation (within a group) either between $\log\Delta H_s$ and the entropy of sublimation of a metal, $S(g)$, or between ΔH_s and the electronic metal density, which, in turn, was expressed via $S(g)$.

It refs. [63a-d], a semi-empirical model was proposed by Ionova, Pershina *et al.* to estimate sublimation enthalpies for all the transition elements. This model appeared as a generalization of different electronic correlations [113–115] used to estimate various properties of metals. For the cohesive energy, E_c , or ΔH_s , the following equation has been proposed [63]

$$E_c = C_{nd}(Z/\gamma), \quad (2)$$

where C_{nd} is an empirically determined coefficient and Z — the atomic number; γ is equal to the following

$$\gamma = \frac{\sum_L (2L+1)_M}{\sum_L [(2L+1)_M + (2L+1)_A]}, \quad (3)$$

where M and A stands for "metal" and "atom", and $(2L+1)$ is the degree of degeneracy of each L state. A character of the dependence of ΔH_s on Z along a transition-element series is defined by $1/\gamma$. Any change in the electronic configuration of the free atom, or participation of the p -orbital in the formation of the metallic state, will influence the character of the dependence of ΔH_s on Z . C_{nd} in Eq. (2) was found to decrease exponentially from the third to

Fig. 3. Calculated sublimation enthalpies of the transition-element metals (from ref. [63]).

the sixth period

$$C_{nd} = ba^x + y, \quad (4)$$

where $x = k\Delta Z$, and ΔZ is the difference in the number of valence electrons between an element of the nd series and a corresponding element of the $3d$ series; $k = 0.1$ is an empirical coefficient, and a , b , and y — parameters, determined from the known ΔH_s for each group of elements [116].

ΔH_s calculated via Eq. (2) for all the d -elements are presented in Fig. 3. They show very good agreement with experiment for the $3d$, $4d$ and $5d$ series. An exponential form of Eq. (4) results in the values of ΔH_s for the transactinides being similar to those for the $5d$ elements. The obtained data indicate no simple increase in ΔH_s in the groups, and in some cases even a reversed trend. Thus, e.g., a decrease in ΔH_s in group 12 results in element 112 being a gas, as it was supposed earlier [37, 104].

IV. Relativistic effects on molecular properties of the transactinide elements

Though the information obtained from relativistic atomic calculations is useful to judge about analogy of the transactinides with the lighter elements in the

periodic table, only molecular calculations can prove whether the properties of their compounds are really in line with the known trends or not.

With the further development of the relativistic molecular orbital (MO) methods, it became possible to predict molecular properties of the transactinides, such as molecular IP, electron affinity (EA), crystal-field and spin-orbit (SO) effects, electronic density distribution and bonding, with sufficient accuracy. Comparing results of relativistic and nonrelativistic calculations enabled one to elucidate the influence of relativistic effects of these properties. Combination of the MO calculations with some other models was useful to estimate and predict some other properties, which could not be calculated directly. The relativistic MO methods and results obtained by their application for the transactinides are described in the following.

A. Relativistic quantum chemical methods for molecules

Traditionally, molecular calculations are divided into two main groups: those where accurate calculations are performed for small molecules, and those, where approximate calculations are done for chemically interesting, more sophisticated systems. The available relativistic molecular methods that can adequately describe the electronic structure of the heavy elements have been overviewed in the literature [66a, 92, 95–99, 117]. Application of modern codes to actinide-containing compounds was demonstrated by Pepper and Bursten [118] and to transactinides before 1996 by Pershina [64]. Therefore, here only their short description will be given arranged roughly in order of the increasing sophistication of the method.

1. Dirac-Fock One-Center Expansion (DF-OCE)

This is a fully relativistic, self-consistent field method with the full (nonlocal) exchange. It is developed as an extension of the numerical atomic DF code for hydride molecules, MH_n , by expanding the potential of the protons in spherical harmonics [120]. Since all the AOs share a common origin, integrals for the radial functions are easily calculated in spherical polar coordinates by numerical methods. The review of the method is given by Desclaux [121]. The method is known to give reasonable bond lengths and force constants, and it was applied to studies of relativistic effects on molecular geometries and bond energies in transition-element compounds [122, 123]. The electronic structures of group 4 and 6 hexahydrides, including RfH_4 and SgH_6 [47, 48] have been calculated using this method.

2. Local Density Functional Methods (LDF)

In this group of methods, the Slater's local exchange potential is used instead of the Hartree-Fock nonlocal exchange. The LDF equations are then solved either by multiple-scattering $X\alpha$ methods, or by various basis-set expansion methods. Due to the approximate exchange-correlation term, correlation effects are treated to a large extent in the LDF methods.

Quasirelativistic Hartree-Fock-Slater (QR-HFS). The method [124] is an extension of the Perturbative Hartree-Fock-Slater (P-HFS) one [125], which was based on the nonrelativistic discrete variational method of Ellis [126]. The method uses analytical basis functions. Relativistic effects of higher orders are taken into account by perturbation operators. In this way, the relativistic corrections to the valence charge density are included. The method gives potential energy curves and was extensively applied to the analysis of bonding and relativistic effects [127,128]. No calculations of the transactinide molecules have been reported.

Quasirelativistic Multiple-Scattering (QR-MS). In this method, the four-component Dirac equation is replaced by an approximate one-component equation. In the Pauli approximate Hamiltonian, the mass-velocity and Darwin terms are included. In some versions of the method [129–131], QR-MS calculations give one-electron non-spin-orbit split MOs; in other versions [132], the SO interaction is put on top of the self-consistent solutions by using the first and second-order relativistic perturbation operator. The radial functions are solved numerically in atomic spheres and plane waves are used between the spheres. The method is mostly used for predicting optical and photoelectron spectra. It gives reasonable orbital energies and descriptions of bonding. Inaccuracies are arising from the "muffin-tin" approximation, but the computational costs are relatively low. First calculations [51] of the electronic structure of the Rf tetrachloride have been performed using this method.

Dirac-Slater Multiple-Scattering (DS-MS). The method is similar to the previous one, but it includes the spin-orbit coupling explicitly: the full Dirac-Slater equations are solved giving four-component MOs. The method gives reliable photoelectron energies, description of bonding, spin-orbit splittings, hyperfine tensors. Slightly different versions of the method are described by Case and Yang [133,134], and Soldatov [135]. The method is reviewed in ref. [136]. Calculations of the electronic structure of the Rf tetrachloride along with its lighter homologs have been published [49].

Dirac-Slater Discrete Variational (DS-DV). Developed by Rosen and Ellis [137, 138], this is a fully relativistic, self-consistent-field method based on the numerical solution of the DF equations, without approximations except for local exchange. Thus, all the relativistic effects including spin-orbit coupling are ex-

plicitly calculated. The method uses four-component basis functions which are transformed into the symmetry molecular orbitals for double point groups using the projection operator method [139] implemented into the program [140].

It provides reliable MOs and orbital energies. Using the Slater transition-state procedure, the ionization potentials and optical spectra can be calculated quite well. The Mulliken population analysis [141] gives the possibility to interpret bonding in terms of ionic (effective charge) and covalent contributions (overlap population, OP). Implementation of the more accurate integration scheme [146], as well as the minimization of the numerical inaccuracies introduced by Bastug [142–146] made it suitable for calculations of binding energies for heavy multiatomic systems [144–147]. Thus, the method offers the possibility to treat chemically interesting and complex systems with sufficient accuracy. As an example, the calculated binding energy for Hg_3^+ is 2.87 eV, which is in good agreement with the experimental value of 2.4 eV [147c]. The work is in progress to improve also the exchange-correlation functional [148,149]. The DS-DV method has been extensively applied to many transition-element molecules and recently to the calculations of a large series of the transactinide-containing molecules [45, 46, 51–62, 68, 230, 231].

3. *Effective Core Potential Methods (ECP)*

The many-electron problem can be efficiently solved at the *ab initio* level by applying the effective core potential (ECP) approach. According to this approximation, frozen inner shells are omitted and in the Hamiltonian an additional potential energy term replaces the core electrons. As a result, the number of basis functions is drastically diminished, and, hence the number of two-electron integrals. Then, the one-electron integrals are solved for the valence basis functions and this additional term by applying *ab initio* schemes at the SCF level or with electron correlation using the configuration interaction (CI), the second-order Møller-Plesset (MP2) perturbation theory and recently the CCSD techniques. Since the variational principle holds for *ab initio* methods, rather accurate total energies can be obtained. The methods and their application are described in refs. [98] and [150].

Quasirelativistic Pseudopotentials (QRPP). In this approximation, atomic calculations, which are used for generating ECP, are two-component wave-functions. The Hamiltonian includes the Darwin and mass-velocity terms, but omits spin-orbit effects. In the Hay-Kahn-Cowan version [151], the spin-orbit effects are included via the perturbation theory after the wave functions have been obtained. The limitation of the method is the absence of the spin-orbit *ab initio* operator. The method has been applied to many transition-metal systems [152], as well as to the actinides [153], and it is implemented into the commercial program "Gaussian 92". For a molecule as heavy as HgCl_2 , the cal-

culated equilibrium bond length (R_e) and dissociation energy (D_e) are 2.301 Å and 2.52 eV [152], respectively, which can be compared with experimental values of 2.29 Å and 4.51 eV [154].

Another version of the QRPP is the quasirelativistic energy-adjusted pseudopotential, which uses energy-optimized valence basis sets [155]. The method is based on quantum mechanical observables for generating ECP. The accuracy of the method for AuH with the CI correlation part is shown in Table 6. In a new version of the method [65], two-component (without averaging over spin-orbit effects) quasirelativistic DF pseudopotentials are generated. The method has been applied to the calculations of group 5 oxides MO, where M = Nb, Ta and Db [65]. Relativistic PP calculations with SO (SOPP) and without SO coupling including correlation at the CCSD level for 111H and 112H⁺, and for 112H⁺, 112F₂ and 112F₄ with the correlation at the MP2 level have been reported recently [67a,b].

Relativistic Core Potentials (RCP). The method is described in detail by Christiansen [156]. The RCPs are generated from all-electron numerical DF atomic calculations. Spin-orbit effects are included in this way from the beginning and full four-component atomic wave functions are obtained [156]. The nonempirical spin-orbit operators were introduced and with some simplifications implemented in the program [157,158]. In this way, the calculation of CI became feasible. Thus, correlation effects can be included through MCSCF (multiconfiguration SCF) or CI calculations. Since the spin states are treated explicitly, the excited states and electronic spectra can be calculated. The calculations are, however, associated with difficulties and high computational costs. RCP results for AuH [159] including electron correlation at the MP2 perturbation theory level are shown in Table 6.

Table 6

Accuracy of different molecular methods for AuH showing importance of relativistic and correlation (CI or MP2) effects

Method	R_e , Å	D_e , eV	Reference
HF	1.831	1.08	[159]
HF+MP2	1.711	1.90	[159]
DF	1.570	1.78	[159]
QRPP+CI	1.504	2.86	[155d]
DK+CCSD	1.525	2.93	[189]
RCP+MP2	1.512	3.08	[160a]
DF+MP2	1.497	3.11	[159]
exp.	1.524	3.36	[196]

The RCPs are presently developed for all the lanthanides, actinides and trans-actinides [160–162]. Calculations of $\text{Sg}(\text{CO})_6$ and 111H with the correlation part at the relativistic CI level have recently been completed [162b].

4. All-electron *ab initio* methods

During recent years, the DHF theory and methodology have been considerably developed. The formulation of the principle of kinetic balance and its extension [163] have given a strong foundation to the employment of the finite basis sets in the DHF calculations. The calculations are based on solution of the Dirac-Fock-Coulomb (DFC) or Dirac-Fock-Breit (DFB) Hamiltonians. In contrast to the ECP and so-called relativistic pseudo-potentials schemes, the DHF methods explicitly incorporate the core orbitals and take into account core-valence exchange. Details of these methods can be found elsewhere [66a, 179, 185].

Among existing programs the following should be mentioned: an earlier Slater-based code for linear molecules of Lee and McLean [164–167], the Gaussian codes for linear molecules of Laaksonen *et al.* [168], for polyatomic molecules of Aerts and Nieuwpoort [169–180], the more recent linear code of Matsuoka [181] and polyatomic codes of Dylla [159, 182–185] and of Saue [186], as well as the numerical code of Pyper and Malli [187, 188]. The amount of calculations performed by using the DHF all electron four-component methods is still small. The computational efforts applied there and costs are tremendous and much higher than for similar quality nonrelativistic systems.

Ab initio relativistic Dirac-Fock SCF calculations for diatomics. The DF SCF *ab initio* approach for diatomics has been developed by Malli and Pyper [187a]. Details of the method are given elsewhere [187b–e]. The basic idea of the method is to express the wave function for the diatomic molecule in terms of the DF numerical atomic functions supplemented with Slater functions. The frozen core and all electron approximations are possible. Electron correlation effects are neglected [188]. Calculations [66a] using this method give predictions of bond length in good agreement with experiment, though they recover only about 50% of the experimental dissociation energies. Calculations of the superheavy diatomic 117Cl have been reported [66a].

Dirac-Fock SCF methods for polyatomics. A four-component SCF DF method has been developed by Saue [186b]. The DIRAC program is set up to do both conventional and direct SCF calculations in a finite (Gaussian) basis based on the DFC-Hamiltonian. An extension for treating correlation effects at the MP2 level exists in the program. Recently, the method has been combined [186d] with the CCSD (correlation) one of Visscher [178]. Calculations of 111H and 117H have been performed without electron correlation [186b,c].

A different version of the DF method with Gaussian basis set has been developed by Dylla *et al.* [159, 182–185]. In contrast to the DIRAC program [186], where expansion of the wave function is done in a scalar one-component basis, a two-spinor basis expansion is used. Calculations with the correlation at the MP2 level have been performed for few small molecules, like AuH (Table 6).

Another DF four-component method for polyatomics, which incorporates correlation effects, is implemented into the MOLFDIR program of Nieuwpoort *et al.* [175–179]. It also uses Gaussian functions for the expansion of the components of the molecular spinors. Correlation effects are included via a multi-reference CI extension [171] and recently at the CCSD level [178]. The method without correlation in its different versions has been applied to a variety of systems [174–176, 180, 184], though with the correlation to still small molecules like PtH (CI) [177] or PtH₂ (CCSD) [178]. The calculations for PtH with the correlation at the CI level give bond length and dissociation energy of 1.518 Å and 2.98 eV, respectively, which show good agreement with experimental values of 1.528 Å and 3.6 ± 0.4 eV, respectively. Typical resources necessary for this kind of calculations are 3–5 GB of disk storage and 20–40 hours of CPU time on a CRAY computer.

DF SCF and DFB calculations without correlation are also performed by Malli *et al.* [66b–e]. For UF₆, the DF and DFB dissociation energies [66e] are 23.53 and 23.27 eV, respectively, (the DF calculations of de Jong and Nieuwpoort give similarly 22.7 eV [180]), which are about 70% of the experimental value of 31.9 eV [193b]. The discrepancy with the experimental value is assigned to the lack of correlation. At present, these DF SCF calculations are performed for group 4, 5 and 6 various halides and oxyhalides, including those of Rf, Db and Sg [66b,g].

5. Douglas-Kroll method

An inexpensive, reliable alternative to the DHF method (if spin-orbit effects are small) was demonstrated to be the second-order Douglas-Kroll (DK) method, developed by Hess [190]. According to the Douglas-Kroll transformation [194], the large and small components are decoupled to second order in the external potential and the spin-orbit terms are neglected in the resulting Hamiltonian. Using one-component wave functions decreases drastically the computational efforts. The DK method has been combined with the Fock-space CC method [83] and applied to the calculations of AuH and 111H [67, 189]. Results for AuH in Table 6 show good agreement with experiment.

In Table 6, comparison of the described methods is given for the case of AuH showing importance of correlation and relativistic effects.

B. The electronic structure and bonding of transactinide gas-phase compounds

1. Transactinide hydrides

Transactinide hydrides, the simplest molecular systems, to which practically all the quantum-chemical methods can be applied without difficulty, were used as models to study influence of relativistic and correlation effects on their properties. First calculations of the electronic structure of the Rf and Sg highest hydrides, RfH₄ and SgH₆, respectively, were performed using the DF-OCE method [47, 48, 195] when studying influence of relativistic effects on bonding and molecular structure of group 4 and 6 compounds. Equilibrium bond lengths and dissociation energies for these molecules as a result of relativistic and nonrelativistic calculations are given in Table 7. The results were shown to be dependent on the basis set selected for the valence orbitals. Discussions of this effect can be found in refs. [99] and [128].

Table 7

Equilibrium distances R_e and dissociation energies D_e (in a.u.) for MH₄ and MH₆. (From refs. [47] and [48]).

Molecule	R_e		D_e		Molecule	R_e		D_e	
	nr.	rel.	nr.	rel.		nr.	rel.	nr.	rel.
TiH ₄	3.244	3.246	0.788	0.783	CrH ₆	3.192	3.181	0.572	0.581
ZrH ₄	3.608	3.615	1.006	0.984	MoH ₆	3.526	3.496	0.777	0.822
HfH ₄	3.626	3.605	0.977	0.999	WH ₆	3.595	3.492	0.796	0.920
RfH ₄	-	3.670	-	0.632	SgH ₆	-	3.607	-	0.980

Relativistic effects were found to decrease the bond lengths in all the hydrides (except TiH₄ and ZrCl₄). They are responsible for the bond lengths of the 4*d* and 5*d* compounds being nearly equal [195]. For RfH₄, the predicted bond length (or covalent radius) is 0.03 Å larger than that of HfH₄, and for SgH₆, it is 0.06 Å larger than that of WH₆. Such a small increase in the covalent radii of the 6*d* elements relative to those of the 5*d* elements is explained, in addition to the relativistic bond contraction, by a large actinide contraction of 0.30 Å, which is mainly a relativistic effect.

Relativistic effects were shown to increase dissociation energies of the hydrides. The increase in the relativistic D_e of the 5*d* relative to the 4*d* compounds was explained by a larger contraction of the relativistic 6*s* and 6*p*_{1/2} orbitals and a larger participation of the more expanded 5*d*-orbitals in bonding (Table 7). For the transactinides, a decrease in D_e and in the force constant k_2 was found when going from HfCl₄ to RfH₄, while in going from WH₆ to SgH₆, k_2 remains essentially constant and D_e increases (Table 7). This trend was supposed to

be caused by relativistic effects [47,48], though an analysis of the contribution of the valence orbitals in bonding in the transactinides has not been given.

Recently, relativistic and correlation effects have been studied for 111H [67] using various relativistic methods (see section IV.A). Results of these calculations are shown in Table 8 [67], with those of the four-component all-electron *ab initio* ones with the electron correlation at the CCSD level still missing. The accuracy of the calculations at the PP level with SO coupling (SOPP) plus the CCSD correlation part was considered to be sufficient to discuss trends in molecular properties.

Table 8

Molecular properties of 111H at various levels of theory. (From ref. [67]).

Method	R_e , Å	D_e , eV	k_e^* , mdyn/Å
NRPP (<i>nr.</i> , <i>uncorr.</i>)	2.017	0.89	1.04
NRPP+CCSD (<i>nr.</i> , <i>corr.</i>)	1.924	1.83	1.11
ARPP ^a (<i>rel.</i> , <i>uncorr.</i>)	1.505	2.32	4.98
ARPP+CCSD (<i>rel.</i> , <i>corr.</i>)	1.498	3.79	4.77
SOPP+CCSD (<i>SO</i> , <i>rel.</i> , <i>uncorr.</i>)	1.504	-	5.04
SOPP+CCSD (<i>SO</i> , <i>rel.</i> , <i>corr.</i>)	1.503	3.05	4.72

^a ARPP - spin-orbit averaged relativistic PP

Relativistic effects were shown to diminish the metal-hydrogen bond distance significantly for AuH and even more for 111H (by 0.42 Å), so that the calculated bond distance of 111H is less than those of both AgH and AuH (Fig. 4). The dissociation energy is relativistically increased by 1.2 eV in 111H (Table 8). An interesting result was a smaller dissociation energy of 111H in comparison with that of AuH. This was attributed to the large SO coupling of the ground state, $^2D_{5/2}$ (and not $^2S_{1/2}$), split by 2.7 eV and resulting in a SO destabilization of 111H. (The SOPP+CCSD result relative to the ARPP+CCSD one shows that D_e decreases from 3.79 to 3.05 eV due to the spin-orbit coupling). Relativistic effects increase the force constant in 111H and change the dipole moment by 4 Debye. Relativistic effects on D_e and R_e have also been discussed for $112H^+$ relative to CdH^+ and HgH^+ [67b] showing a similarity with the case of 111H. Nonadditivity of relativity and correlation has been demonstrated.

Fig. 4. Nonrelativistic and relativistic molecular properties for the group 11 series of hydrides. The data for CuH, AgH, and AuH are from refs. [196], [159], [189] and [194e]. (From ref. [67a]).

2. Transactinide Halides

Highest halides of Rf, Db and Sg are volatile compounds formed [6–9, 11, 13] by analogy with the lighter homologs in the corresponding groups. Stability of the lighter compounds is known to decrease from group 4 to group 6, and starting with group 7, the highest halides are not stable. The stability of the halides with metals in the maximum oxidation state also decreases in going from fluorides to chlorides, and further to bromides and iodides [197]. Due to high temperatures applied in the gas-phase chromatography experiments on studying volatility of the transactinide halides, predictions of their thermochemical stability were very important.

Fluorides. The fluorides of the transactinides have not yet been studied experimentally, though there was quite a number of theoretical investigations. In group 4, the electronic structure of RfF₄ and its homologs ZrF₄ and HfF₄ has been calculated using the all-electron *ab initio* DF method [66b]. The similarity of the Rf compound with the lighter homologs was indicated.

For group 6 highest fluorides, MoF₆, WF₆ and SgF₆, the electronic structure calculations have been performed by Rosen *et al.* [46] using the DS-DV method. Results of the calculations have shown the electronic structure of SgF₆ to be similar to those of the lighter homologs. By applying the transition state procedure, the first IP for SgF₆ of 15.4 eV was given.

Ab initio all-electron calculations [66b] have been performed for WF_6 and SgF_6 giving 19.51 and 18.20 eV, respectively, for the dissociation energies, and 1.82 and 1.92 Å, respectively, for the equilibrium bond distances.

DS-DV calculations have been performed for 110F_6 [45a,b]. A similarity in properties between 110F_6 and PtF_6 was assumed on the basis of the calculated close values of their IP. Some optical transitions were predicted for 110F_6 , which are important for detecting this compound with the use of lasers in resonance ionization spectroscopy [198], or resonance fluorescence [199]. *Ab initio* DF calculations were also reported for 110F_6 [66b].

The SOPP calculations with the correlation at the MP2 level were published for 112F_2 and 112F_4 [67b]. 112F_4 was shown to be stable with respect to the decomposition into 112F_2 and F_2 due to relativistic effects. As a consequence, the oxidation state +4 was predicted to be accessible for element 112 in the gas phase.

Chlorides and bromides. The electronic structure of the Rf highest chloride, RfCl_4 , has been studied in quite a number of publications, since this was one of the first molecules of the transactinides produced and investigated experimentally. The following methods have been applied to calculations of the electronic structure of MCl_4 , where $\text{M} = \text{Ti}, \text{Zr}, \text{Hf}$ and Rf : QR-MS [51], DS-MS [49], the DS-DV [50,61], and the all-electron *ab initio* DF [66b]. Results obtained by application of these methods agree that the electronic structure of RfCl_4 is similar to that of HfCl_4 (and not to that of PbCl_4), and that the bonding is typical of the transition *d*-element compounds. There are some unessential discrepancies in effective charges and overlap populations (Table 9).

Table 9

Effective charges on the metal atom (Q_M) and overlap populations (OP) in MCl_4 , where $\text{M} = \text{Zr}, \text{Hf}$ and Rf , obtained as a result of different calculations

Molecule	Q_M			OP
	DS-MS ^a	DS-DV ^b	DF ^c	DS-DV ^b
ZrCl_4	2.36	1.18	1.90	0.48
HfCl_4	2.34	1.04	1.44	0.55
RfCl_4	2.30	1.07	1.40	0.57

^a Ref. [49]; ^b ref. [61]; ^c ref. [66b].

The results have shown an increase in the covalence (OP) and a decrease in the ionicity (Q_M) with increasing atomic number of metal. This comes at the expense of an increasing participation of the valence $ns_{1/2}$ and $np_{1/2}$ orbitals in bonding. Estimates of the bond energies for the MCl_4 molecules as a sum of the ionic and covalent parts have been given showing an increasing stability with increasing atomic number of the metal [61].

The DF SCF dissociation energies of 16.32, 14.26 and 15.55 eV have been calculated [66b] for ZrCl_4 , HfCl_4 and RfCl_4 , respectively, where the last value is for the $7s^2 6d^2(\text{Rf})$ basis set. These values are lower than the experimental (thermochemical) ΔH_{diss} of 20.35 (or 20.05 [154]) and 20.55 eV for ZrCl_4 and HfCl_4 , respectively (see ref. [57]), which is explained by the lack of correlation in the DF method. (The difference between D_e and ΔH_{diss} should be kept in mind). Optimized bond lengths are 2.36, 2.32 and 2.32 Å for the tetrachlorides of Zr, Hf and Rf, respectively, showing good agreement with experimental values for the first two compounds of 2.32 and 2.316 Å, respectively [200a].

The electronic structure of the highest chlorides and bromides of Db, along with those of its group 5 homologs Nb and Ta, and influence of relativistic effects have been investigated in refs. [52, 53, 57] and [61] using the DS-DV method. Energy eigenvalues for MCl_5 ($\text{M} = \text{Nb}$, Ta and Db) as a result of the relativistic and nonrelativistic calculations [52, 57] are shown in Fig. 5 indicating that the electronic structure of the Db compound is similar to those of Nb and Ta.

The eigenvalues of Fig. 5 elucidate the opposite trends in the relativistic and nonrelativistic values in going from the Ta to the Db compound: relativistic IP (HOMO) and the energy gap between the highest occupied MO (HOMO) and the lowest unoccupied MO (LUMO), ΔE , increase, while the nonrelativistic IP and ΔE decrease. For EA, the relativistic values decrease from the Ta to the Db compound, while the nonrelativistic values increase. Thus, relativistic effects are responsible for the increase in IP, the decrease in EA, the increase in ΔE , in the energies of the charge-transfer transitions, $E_{\pi-d}$, and in E_{SO} in the group. The reason for that is a relativistic destabilization of the valence $6d$ orbitals, as it is reflected in Fig. 1.

Table 10

Effective charges on atoms (Q_M) and total overlap populations (OP) for MCl_5 as a result of relativistic (rel.) and nonrelativistic (nr.) calculations. (From ref. [57]).

Molecule	Q_M		OP	
	nr.	rel.	nr.	rel.
VCl_5	1.12	1.12	1.70	1.70
NbCl_5	0.97	0.92	1.92	2.04
TaCl_5	1.12	0.95	2.09	2.49
DbCl_5	1.19	0.81	1.82	2.60

The same opposite effects were found in the relativistic and nonrelativistic charge density distribution and bonding (Table 10). (The relativistic charge-density distribution differs from the nonrelativistic distribution due to the electron reorganization at a given interatomic distance and due to its rela-

Fig. 5. Energy level diagrams for NbCl_5 , TaCl_5 and HaCl_5 (Ha-element 105) as a result of the HFS nonrelativistic (nr) and DS-DV relativistic (rel) calculations. (From ref. [57]).

tivistic change). Due to the relativistic stabilization and contraction of the valence ns and $np_{1/2}$ orbitals with increasing Z in the group, their involvement in the bonding increases giving rise to an increase in the covalence (OP) and decrease in the ionicity (Q_M). Thus, the relativistic trends in OP and Q_M are just opposite to the nonrelativistic ones from Ta to Db, as it is seen from Table 10. Probably, without relativity DbCl_5 would be as unstable as VCl_5 .

Relativistic effects are responsible for the increasing stability of the maximum oxidation state in the group. Using a linear correlation between relativistic energies of the charge-transfer transitions $E_{\pi-d}$ (increasing in the direction to Db) and reduction potentials, corresponding to the transition from the +5 to the +4 state, $E^0(\text{V} - \text{IV})$ for Db of -1.0 V have been obtained indicating that the stability of the +5 oxidation state changes in the following way in the group: $\text{V} < \text{Nb} < \text{Ta} < \text{Db}$. Without relativity Db^{5+} would have been less stable than Nb^{5+} (Fig. 6).

The electronic structure of group 6 hexachlorides MCl_6 ($\text{M} = \text{Mo}, \text{W}$ and

Fig. 6. Correlation between redox potentials $E^0(V - IV)$ and relativistic energies of the lowest charge-transfer transitions in MCl_5 ($M=V, Nb, Ta$ and element 105, Ha). The nonrelativistic values for Ha is shown by an open circle.

Sg) has been calculated using the DS-DV method [61]. The obtained data are indicative that the Sg hexachloride is similar to the W hexachloride. The covalence (OP in Table 11) does not, however, increase in going from the W to the Sg chloride, in contrast to group 4 from the Hf to the Rf chloride, or to group 5 from the Ta to the Db chloride. A conclusion about a weaker bonding in $SgCl_6$ in comparison with that in WCl_6 was therefore drawn due to the smaller both Q_M and OP [61]. Recently, direct calculations of the equilibrium bond lengths and binding energies of $MoCl_6$, WCl_6 and $SgCl_6$ have been performed [64b] using the recent version of the DS-DV method (Table 12). The calculated potential energy curve for $SgCl_6$ is shown in Fig. 7. The obtained D_e are in very good agreement with experimental (thermochemical) values for the Mo and W compounds, though the calculated R_e are less satisfactory (Table 12). According to these results, a decomposition of $SgCl_6$ at high temperatures has been proposed taking into account the following arguments [61,64b]: Since $MoCl_6$ is not stable at the room temperature, and WCl_6 decomposes at the boiling point of $346^\circ C$ both with the formation of MCl_5 , the seaborgium hexachloride having a weaker or equal M-Cl bonding to that of WCl_6 would obviously also decompose. The enthalpy of the reaction $SgCl_6 \Rightarrow SgCl_5 + 1/2Cl_2$ has been estimated as 22.3 kcal/mol [61]. This makes $SgCl_6$ unsuitable (to be kept in the VI valence form) for the gas-phase chromatography experiments run at temperatures above $1000^\circ C$.

Calculations of the electronic structure of MCl_6 ($M = Mo, W$ and Sg) have also

Table 11

Effective charges (Q_M) and overlap populations (OP) for one metal-chlorine bond for group 4, 5 and 6 highest chlorides. (From ref. [61]).

	MCl ₄		MCl ₅		MCl ₆	
Q_M	Zr	1.18	Nb	0.93	Mo	0.79
	Hf	1.04	Ta	0.95	W	0.74
	Rf	1.07	Db	0.81	Sg	0.59
OP(M-Cl)	Zr	0.48	Nb	0.41	Mo	0.36
	Hf	0.55	Ta	0.50	W	0.46
	Rf	0.57	Db	0.52	Sg	0.45

Table 12

Results of the calculations of D_e and R_e for MCl₆ (M = Mo, W and Sg. (From ref. [64b]).

Method	MoCl ₆	WCl ₆	SgCl ₆	Reference
D_e , eV				
DS-DV	20.97	22.18	20.05	[64b]
exp. ^a	19.29	21.65	(20.11) ^b	(see ref. [61])
R_e , Å				
DS-DV	2.33	2.36	2.45	[64b]
exp.	2.254	2.26	(2.39) ^b	[201a,c]

^a Obtained via the Born-Haber cycle; ^b extrapolated from the experimental values for MoCl₆ and WCl₆ using calculated DS-DV values for MCl₆ (M = Mo, W and Sg) [64a]

been performed using the DF method [66b]. Results have shown an increase in the M-Cl bond strength with increasing atomic number of the metal (6.73, 11.49 and 12.71 eV for MoCl₆, WCl₆ and SgCl₆, respectively). Relativistic effects proved to enhance the binding energy of SgCl₆ by 3.31 eV.

Comparison of group 4, 5, and 6 highest chlorides. The calculations of the electronic structure of group 4, 5 and 6 highest chlorides have shown the groups to be very similar with the bonding changing in a similar way with increasing Z. The halides of Rf, Db and Sg have similar energy level structures (Fig. 8), with the MO being more stabilized with increasing atomic number of the metal. The energy gap ΔE between the occupied and vacant *d*-levels decreases from 4.98 to 3.25 and to 2.46 eV for RfCl₄, DbCl₅ and SgCl₆, respectively.

Effective charges and total overlap populations for a single M-Cl bond of these compounds are given in Table 11. The obtained OPs reflect experimen-

Fig. 7. Potential energy curve for SgCl_6 . (From ref. [64b]).

tally found regularities [197,201-207]: an increase in the metal-chlorine bond strength of the $5d$ relative to the $4d$ compounds, and a decrease in it in going from group 4 to group 6. The lowest value of OP for MoCl_6 corresponds to its instability. Due to the highest OP and a relatively large ionic contribution to bonding (Q_M), RfCl_4 is the most stable in group 4, while a decrease in OP(M-Cl) in group 6 from WCl_6 to SgCl_6 results probably in a lower stability of SgCl_6 than that of WCl_6 , which was also confirmed by direct calculations of D_e [64b]. Thus, in the row RfCl_4 , DbCl_5 , and SgCl_6 , the tendency to a decrease in the M-Cl bond strength known for the $4d$ and $5d$ lighter homologs will be even more pronounced. The same has been shown by formation enthalpies of these halides obtained via the Born-Haber cycle [61] using the calculated ΔH_s of metals [63d].

Besides a decrease in the M-Cl bond strength in the highest transactinide chlorides with increasing atomic number of the metal atom, the stability of the maximum oxidation state also decreases. This is seen from a linear correlation between calculated (via the transition-state procedure) energies of the charge-transfer transitions in MCl_n , $E_{\pi-d}$, corresponding to transitions from the highest to the next lower oxidation states, and related redox potentials E^0 (Fig. 9) for RfCl_4 , DbCl_5 , and SgCl_6 . (See also section V).

Other chlorides. Diatomics of heavy elements, including 117Cl , have been studied in ref. [66a] using the DF method. The results have shown a relativistic increase in the bond strength up to 0.70 eV, in comparison with the non-relativistic value of 0.009 eV. The nonrelativistic bond length was found to be 4.99 bohr, while the relativistic value is 5.25 bohr. Thus, the results predicted a larger bond distance, smaller force constant and about two orders of magnitude greater binding energy for 117Cl in the relativistic case compared

Fig. 8. Energy level diagrams for the highest chlorides of Rf, element 105, Ha, and Sg, as a result of the DS-DV calculations. (From ref. [61]).

to the nonrelativistic one.

3. Transactinide Oxides

One of the interesting questions was the influence of relativistic effects on the ground state of open-shell compounds of the transactinides, e.g., Rf and Db monoxides, though these compounds have not yet been produced. For their lighter homologs, HfO and TaO, relativistic effects are known to be responsible for the stabilization of the ground state with paired electrons, like $^1\Sigma^+$ in HfO and $^2\Delta_{3/2}$ in TaO in contrast to the $^3\Delta$ and $^4\Sigma^-$ states of TiO and NbO, respectively, having unpaired electrons [205, 208, 209]. In addition, the knowledge of the metal-oxygen bonding in these systems can be useful to understand the bonding in more complex oxyhalides compounds, which are often formed simultaneously with the highest halides.

In ref. [210], a $^2\Delta_{3/2}$ ground state electronic configuration for DbO was proposed assuming that relativistic stabilization of the $7s$ and $7p$ orbitals in DbO results in an increase in $np\sigma 2s\sigma + np\sigma 2p\sigma + np\pi 2p\pi$ interaction. The dissociation energy for DbO has been estimated using a model described in ref. [211]. Obtained D_e shows a weaker bonding in DbO than that in TaO.